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ORIGINAL PAPER

Direct Insight into Near-frictionless Behavior Displayed by Diamond-like Carbon Coatings in Lubricants

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Abstract Surface physical properties and chemical states on a nanometer scale were investigated to provide a direct insight into the mechanism of near-frictionless performance displayed by diamond-like carbon (DLC) coatings in engine oil lubricants. A mechanism was revealed by combining nanoprobe methods with surface chemical analysis. The near-frictionless behavior observed in the lubricants was found to stem from strong repulsive force between hydrogen-terminated carbon chains, originating from the bonding of oil additive molecules on the DLC coating surface producing sliding contact between H-terminated alkyl chain layers.

Keywords AFM · Chemical analysis techniques · Coatings · Friction-reducing · XPS · Automotive · Boundary lubrication friction · Nanotribology · Contact mechanics · Diamond · Carbon · Organic esters · Friction mechanisms · Surface modification

In the last few years, an impressive finding was made that low-cost, low-wear, chemically stable diamond-like carbon (DLC) films can exhibit a superlow friction performance, not only observed in the sliding of DLC film containing a large amount of hydrogen in a dry nitrogen atmosphere [1], but also seen in the sliding of hydrogen-free DLC film under an oil lubricant condition [2–4] for a wide range of industrial applications. The friction reduction mechanism has attracted widespread interest with regard to scientific understanding for putting this finding to practical use. However, several researches for the case exhibited only in a dry nitrogen atmosphere were reported [5–8]. Dickrell et al. proposed a closed-form time- and position-dependent model for fractional coverage, based on the adsorption of environmental contaminants and their subsequent removal through sliding contact [5, 6]. Erdemir suggested a dipole configuration that gives rise to repulsion rather than attraction between the hydrogen-terminated sliding surfaces of the DLC films [7]. Dag et al. modeled the sliding friction between hydrogenated diamond surfaces for explaining the superlow friction originating from the steady repulsive interaction between the sliding surfaces [8]. In any case, there is no direct analytical evidence showing the adsorbed contaminants or the dipole configuration formed on sliding surfaces to support these friction reduction models.

Our recent studies have demonstrated that nanometer-scale properties, referred to here as analytical properties, such as the nanostructure, nanoproperties, and nanofunctions of the surface materials act as extremely important factors in controlling macro-scale tribological performance [9–12]. For the purpose of elucidating these controlling factors and their correlations, it is indispensable to obtain direct surface information, including various structural, physical, and chemical properties or characteristics on a nanometer scale without any influence from surface roughness. Probing techniques such as atomic force microscopy (AFM) and the nanoindentation method are powerful tools for ascertaining the real nature of sliding surface [9–12].

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In this letter, our effort to find the origin of the superlow friction behavior is focused on the differences in surface roughness, nanostructure, nanoscale friction coefficient, and the chemical state between the sliding and nonsliding surface areas. These nanoscale controlling factors are investigated by using AFM, the AFM phase-image technique, nanoprobe-sliding measurement, and X-ray photonelectron spectroscopy (XPS). Usually, the type of the adsorbent layers formed on the sliding surface in an engine oil is more stable in air than that formed under an inert gas condition [5, 6]. This letter focuses on the surface chemical changes that appear to result in the super-lubrication behavior displayed in an engine oil, and the elucidated mechanism of the friction reduction is also discussed in relation to the friction behavior exhibited under an inert gas condition.

The sliding surface exhibiting a superlow friction coefficient of 0.006 was prepared by sliding a pin on a hydrogen-free DLC film coated on a Si(100) wafer. The pin was made of bearing steel and the DLC coating on the Si wafer was grown by physical vapor deposition. Poly-alpha-olefin based oil containing a friction modifier additive of glycerol monooleate ester (PAOES1 oil) was introduced directly at the beginning of the sliding test. The test was performed under a pressure of 0.2 GPa at a rotational speed of 0.03 m/s at 353 K for 30 min [2, 4]. The DLC film coated on the Si wafer makes the sliding surface flat enough for surface analysis, as compared with a DLC film coated on the normally used steel disk.

Figure 1 shows AFM height and phase images of the sliding and nonsliding areas. By comparing the topographies of the areas, it was noted that some shallow surface flaws formed and the surface became rougher after the sliding test. Most importantly, it was found that the phase images did not reveal any distinct features on the nonsliding surface, but island structures with a size of 20–40 nm and a height of 1.5–2.5 nm formed on the sliding surface. These observations indicated that surface roughness was not a factor contributing to the friction reduction. Since the observed surfaces were ultrasonically cleaned with hexane prior to the AFM observations, the islands are thought to be chemically adsorbed on the sliding DLC surface, with the result that they cannot be removed by solvent cleaning.

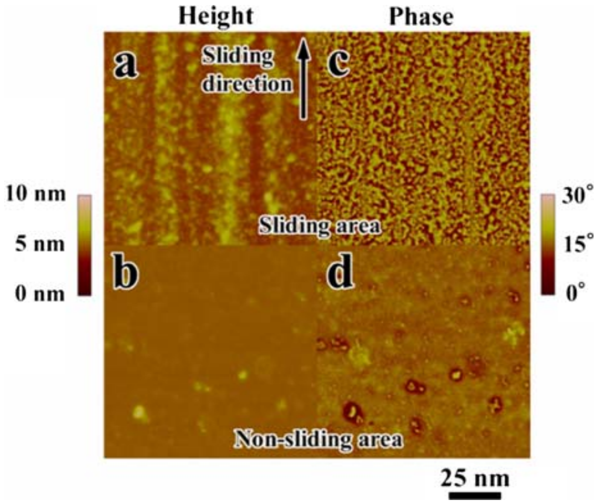

Fig. 1 Typical AFM height and phase images of the hydrogen-free DLC films after the pin-on-disc sliding test: (**a**) height and (**c**) phase of the sliding area; (**b**) height and (**d**) phase of the nonsliding area

These thin adsorbed islands, which only formed on the sliding surface, were examined to see if they possessed low shear force or not. That was done using nanoprobe-sliding measurements based on a nanoindention technique to detect any difference in the nanoscale friction coefficient between the sliding and nonsliding areas. The nanoscale friction coefficient can be abbreviated to the nanofriction coefficient, which is known to represent friction intrinsic to the surface materials because the measurement area is small enough not to be without being influenced by surface roughness [10]. In the measurement, a conical diamond tip with a cone angle of 60° and a radius of about 1 μm was used. Lateral force and normal displacement were obtained by applying various levels of constant normal force ranging from 300 to 2000 μN with a lateral displacement of less than 400 nm. Figure 2 shows the nanofriction coefficient distributions relative to the normal force under elastic contact for the sliding and nonsliding areas. As the contact depth and the contact area normal to the nanoprobe-sliding direction increased with the normal force, the nanofriction coefficients for both areas were found to increase with the normal force. However, it is noteworthy that the sliding areas displayed much lower nanofriction coefficients than the nonsliding areas independent of the normal force. The nanoprobe-sliding measurements thus verified that the chemical adsorbents formed on the sliding areas possessed a low friction nature. As this low friction nature was sustained even at ultra-high contact pressures in a range from 0.23 to 4.0 GPa, the chemical adsorbents were inferred to be strongly bonded to the sliding DLC surface.

To understand why the ultra-thin adsorbent islands displayed a low friction nature, it indispensable to know their constituent chemicals and bonding state with the hydrogen-free DLC surface. As the adsorbent islands were ultra-thin with a thickness less than 2.5 nm, two different take-out angles of 15° and 75° were used for XPS surface analysis to detect photoelectrons from the shallow and deep ranges at detection depths of 2 nm and 5 nm, respectively. As shown in the XPS C1s spectra in Fig. 3, alkyl chains of $-(CH_2)_n-$ representing component parts of the oil additives were detected in both the sliding and nonsliding areas from the shallow and deep detection ranges. The oil additive

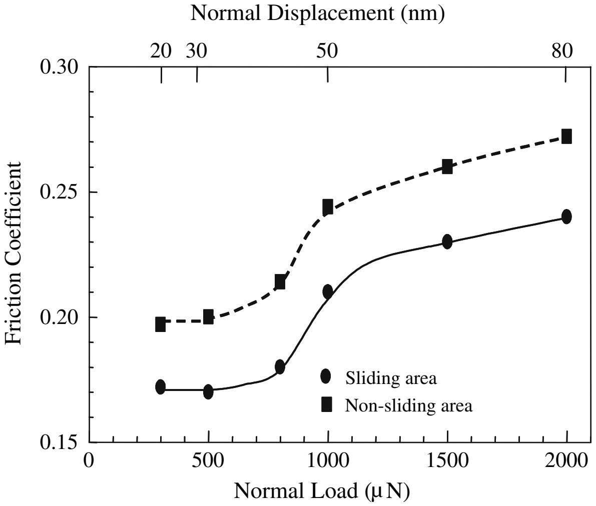

Fig. 2 Nanoprobe-sliding measurements revealing nanofriction coefficient distributions relative to the normal load and the normal displacement obtained from the sliding and non-sliding areas of the hydrogen-free DLC films after the pin-on-disc sliding test

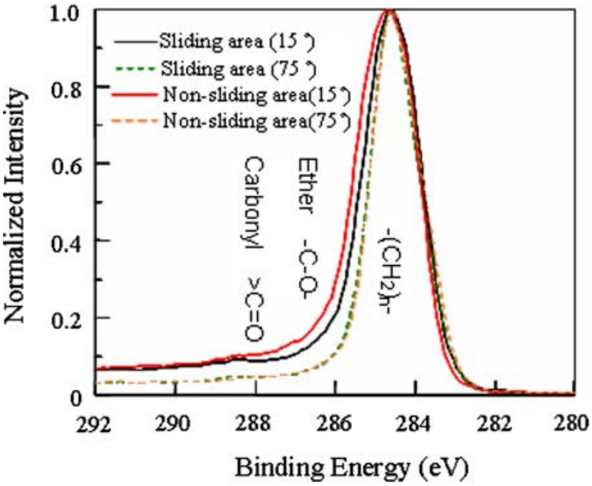

Fig. 3 XPS C1s spectra detected at two different take-out angles of 15° and 75° from the sliding and non-sliding areas of the hydrogen-free DLC films. Peak intensities of the –$(CH_2)_n$– alkyl chains were normalized to determine the difference in chemical states between the sliding and non-sliding areas

molecules of glycerol monooleate ester $C_{17}H_{33}$–COO-CH_2–CH(OH)–CH_2(OH) were found to be distributed on both the sliding and nonsliding areas. It was noted that the bonding energies at carbonyl O=C< and ether –C–O– always displayed lower strength in the sliding areas than in the nonsliding areas in the shallow detection range, but no difference was found in bonding energy between the sliding and nonsliding areas in the deep detection range. These observations are a direct indication that in the sliding area, the additive molecules were assembled and bonded with C atoms on the hydrogen-free DLC surface through the agent of O atoms of hydroxyl –OH to form a monomolecular layer as illustrated in Fig. 4. This configuration allowed the carbonyl O=C< and ether –C–O– groups to be located at the interface just below the monomolecular layer with a thickness of about 2 nm, resulting in lower O=C< and –C–O– bonding energy, as compared with that obtained in the nonsliding area where the additive molecule chains were randomly and physically absorbed on the surface. As a result, the monomolecular lubricant layer was formed of alkyl chains terminated by H atoms as shown in Fig. 4. The superlow friction behavior originated from the sliding contact between H-terminated alkyl chain layers, where the strong repulsive force between H-terminated C chains lowered the boundary friction coefficient to the superlow level.

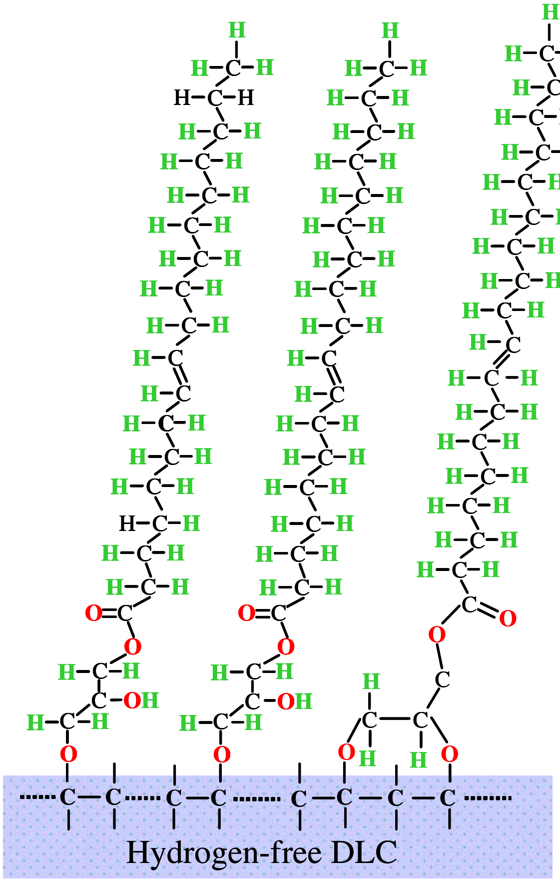

Fig. 4 A model based on XPS analysis that directly reveals the nature of the superlow frictional behavior. Alkyl chains connect with C atoms on the fresh sliding DLC surface through the agent of O atoms of hydroxyl –OH to form the lubricant layer; the sliding contact between H-terminated alkyl chain layers is characterized by strong repulsive force between H atoms

This friction reduction mechanism in an oil lubricant also gives an insight into the superlow friction phenomena displayed by a hydrogen-containing DLC film sliding in inert gases. Direct analytical insight substantiates the assumption proposed by Erdemir et al. that the steady repulsive interaction between the hydrogen-terminated DLC surfaces can result in a friction reduction to the superlow level [7]. Thus the friction reduction mechanisms in both cases are fundamentally the same. From the viewpoint of practical application, however, we still need to discuss the difference between the superlow friction behavior exhibited by a hydrogen-free DLC film sliding in an oil lubricant and that of a hydrogen-containing DLC film sliding in inert gases. In the former case, the sliding contact between H-terminated alkyl chain layers is less influenced by the sliding environment. In the latter case, however, the hydrogen-terminated DLC contact surfaces are easily contaminated by environmental changes. The extent of capillary force due to moisture precipitation and the extent of the attractive force due to contaminant adsorption on the sliding surface can cause the superlow friction performance to be lost. Using the alkyl-terminated DLC contact surface instead of the hydrogen-terminated DLC contact surface is a very promising way to obtain steady superlow friction performance.

The elucidated friction reduction mechanism in an oil lubricant also provides an insight into how to improve superlow friction behavior to a lower level and how to reduce the cost of obtaining superlow friction performance. With regard to the former question, lengthening the alkyl chains and densifying the active sites for chemical adsorption of the alkyl chains may increase the contact area between H-terminated alkyl chains, resulting in a much lower friction level. As for the latter issue, terminating alkyl chains on hydrogen-containing DLC films is a formidable challenge because the cost of the hydrogen-containing DLC coating grown by a chemical vapor deposition process is lower than that of the hydrogen-free DLC coating grown by a physical vapor deposition process. In both films, contaminants adsorbing onto the DLC film can be removed to form a fresh sliding DLC surface by the sliding test. However, the hydrogen-free DLC film contains numerous chemical sites due to the extent of the dangling bonding of C atoms, resulting in alkyl chains easily connected with C atoms on the fresh sliding DLC surface through the agent of O atoms of hydroxyl –OH to form an alkyl layer. In contrast, with the hydrogen-containing DLC film, the dangling bonds of C atoms are terminated by H atoms and there are fewer active sites on the fresh sliding DLC surface for connecting alkyl chains. Doping the hydrogen-containing DLC film with some active elements and modifying the surface are ways of increasing chemical active sites for bonding assembled alkyl chains.

The findings described here indicate a way of directly obtaining physical properties of the nanometer-scale surface and chemical states of sliding surfaces, which are extremely important factors in controlling macro-scale tribological performance. They show that the superlow friction behavior displayed in an oil lubricant originated from the sliding contact between alkyl chain layers, in which strong repulsive force between H-terminated C chains lowered the boundary friction coefficient to the superlow level. These findings offer a new insight into the superlow friction behavior observed not only in a lubricant but also in inert gases or in an ultra-high vacuum, as well as an insight into ways of improving the superlow friction behavior to a lower level and reducing the cost of obtaining superlow friction performance.

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