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A fundamental mechanism for carbon-film lubricity identified by means of *ab initio* molecular dynamics

Seiji Kajita [a, b, *], M.C. Righi [b, c, **]

[a] Toyota Central R&D Labs., Inc., 41-1, Yokomichi, Nagakute, Aichi, 480-1192, Japan
[b] Dipartimento di scienze Fisiche, Informatiche e Matematiche, Universita' di Modena e Reggio Emilia, Via Campi 213/a 41125 Modena, Italy
[c] Istituto Nanoscienze, CNR-Consiglio Nazionale delle Ricerche, I-41125, Modena, Italy

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ABSTRACT

Different hypotheses have been proposed to explain the mechanism for the extremely low friction coefficient of carbon coatings and its undesired dependence on air humidity. A decisive atomistic insight is still lacking because of the difficulties in monitoring what actually happens at the buried sliding interface. Here we perform large-scale *ab initio* molecular dynamics simulations of both undoped and silicon-doped carbon films sliding in the presence of water. We observe the tribologically-induced surface hydroxylation and subsequent formation of a thin film of water molecules bound to the OH-terminated surface by hydrogen bonds. The comparative analysis of silicon-incorporating and clean surfaces, suggests that this two-step process can be the key phenomenon to provide high slipperiness to the carbon coatings. The water layer is, in fact, expected to shelter the carbon surface from direct solid-on-solid contact and make any counter surface slide extremely easily on it. The present insight into the wettability of carbon-based films can be useful for designing new coatings for biomedical and energy-saving applications with environmental adaptability.

1. Introduction

Carbon-based films, as (poly)crystalline diamond and amorphous diamond like carbon (DLC), have attracted great interest from both the industry and scientific community due to their exceptional physical, chemical, biomedical, mechanical and tribological properties [1,2]. Tribologically, carbon films provide some of the lowest known friction and wear coefficients without any environmental pollution related to their use [3–6]. However, the widespread application of carbon films has been hindered by a long-standing problem related to the influence of air humidity on their tribological performances [7–14]. In DLC systems, for example, both highly positive and negative effects of humidity on the friction coefficients and wear rates have been reported even in the same type of tribological test conditions [11,12]. This uncontrolled behavior is most likely the result of chemical reactions activated at the buried sliding interface interacting with water molecules. The chemical compositions of the carbon film and its hydrogen content can deeply alter the surface reactivity and friction [13,14]. Indeed, friction reduction by moisture has been attributed to surface passivation by water chemisorption, which reduces the adhesion with a counter surface [9,13,15–19]; especially, hydrophilic hydroxyl groups are considered to play a crucial role in reducing the friction [9,20–22]. In addition to the passivation, recent nano-scale experiments suggested another possible atomic mechanism to explain the extremely low friction of carbon-based film, which is connected to the presence of water molecules confined at the friction interface [10,23–25]. By means of atomic force microscope (AFM) measurements it has been uncovered the presence of an adsorbed water layer, few molecules thick, which may function as boundary lubricant on DLC films [10]. A friction force measurement showed that the viscosity of the confined water layer is more than 10^8 times greater than that of bulk water [23]. A nanoconfined water layer has been also considered to explain the lubrication mechanisms of steel by glycerol [25–27] and polymer brushes [28].

The formation of a confined water layer seems favored by the incorporation of silicon atoms into the carbon matrix in a suitable dosing [29–31]. Si-doped DLC (Si-DLC) and SiC show, in fact, more

* Corresponding author. Toyota Central R&D Labs., Inc., 41-1, Yokomichi, Nagakute, Aichi, 480-1192, Japan.
** Corresponding author. Dipartimento di scienze Fisiche, Informatiche e Matematiche, Universita' di Modena e Reggio Emilia, Via Campi 213/a 41125 Modena, Italy
E-mail addresses: fine-controller@mosk.tytlabs.co.jp (S. Kajita), mcrighi@unimore.it (M.C. Righi).

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stable and lower friction coefficients in water and humid environments than undoped DLC. Initially, the low friction mechanism of the Si incorporating carbon films was believed to be completely different from that of Si-free films and attributed to silica-sol wear debris resulting from the oxidation of silicon fragments by water vapor [8,32–37]. However, films incorporating a low amount of silicon present very low friction in spite of the absence of any significant wear [38,39]. Several authors have reported that water can dissociate directly at the silicon sites incorporated at the carbon surface leading to the formation of hydroxyl groups at these sites [12,40–44]. By means of first principles calculations of water adsorption we showed that the hydroxyl termination enhances the surface hydrophilicity [45], in agreement with experimental observations [46,47]. Kasuya et al. performed resonance shear measurements for evaluating the properties of water confined between silica surfaces with different concentrations of silanol (Si–OH) groups at the surface, and observed ice-like water on the surface terminated with a high concentration of Si–OH, which could provide lubricity under high normal pressure more than a low concentration of Si–OH groups [48]. The formation of a structured water layer upon Si–OH termination of the carbon surface was also observed by classical molecular dynamics (MD) simulations [49].

Despite the growing interest in understanding the atomistic mechanisms for the low friction and wear of carbon-based coatings, our present understanding is limited by the difficulty in monitoring the buried sliding interface. A direct access by experiments is, in fact, extremely challenging and molecular dynamics simulations based on empirical force fields are typically inadequate for an accurate description of chemical reactions occurring in conditions of enhanced reactivity. Here we apply large-scale *ab initio* MD simulations that realistically describe the water/surface interaction [45,50,51], and provide *in situ*, real-time monitoring of tribochemistry processes [17]. Thanks to a comparative study of Si-incorporating and pure diamond surfaces we highlight the pivotal role of the stress-assisted surface hydroxylation and the subsequent formation of a nano-confined layer of water molecules strongly bound to the surface.

2. Method

We perform *ab initio* MD simulations based on the Car Parrinello method [52] by means of the pseudopotential/plane-waves computer code included in the QUANTUM ESPRESSO package [53], which has been modified by our group in order to simulate tribological systems [17]. Interfaces are modeled by periodic supercells of 15.1 Å × 10.1 Å × 20.0 Å dimensions, containing two diamond slabs 6 layers thick, with (6 × 4) in-plain size. The diamond surface presents a (2 × 1) reconstruction constituted of dimers that gives rise to alternating rows and trenches of sp^2- and sp^3-bonded carbon atoms. Bonds with this different hybridizations are also present in DLC [54], therefore our model aims at mimicking the *local* reactive sites of the DLC surface. The effects of larger-scale features, such as steric effects due to the roughness of DLC surfaces [21], are not taken into account in the present model. The large number of atoms included in our system (up to 378) and the simulated time intervals, about 10 ps for each trajectory, render our simulations computationally very demanding, in particular they required about 100 k cpu hours highly parallel supercomputers per each trajectory, which points out the importance and the complexity of the current work.

The electronic structure is calculated by means of the density functional theory (DFT) with the Perdew–Burke–Ernzerhof (PBE) approximation for the exchange correlation functional [55]. The ionic species are described by ultrasoft pseudopotentials [56]. The electronic wavefunctions are expanded in a plane-wave basis set with a cut-off energy of 25 Ry, and the Brillouin zone is sampled at the Gamma point.

In the CP dynamics, the ionic and electronic degrees of freedom evolve simultaneously, a fictitious mass of 450 a.u. is assigned to the electrons and the equations of motions are integrated with the Verlet algorithm with a time step of 5 a.u. = 0.12 fs. Deuterium is used instead of hydrogen so as to avoid unphysical coupling between electronic and ionic degrees of freedom in the concurrent execution of the time evolution. The temperature of the system is kept constant at 300 K by means of a Nosé-Hoover thermostat composed by double chains with frequencies of 30 THz and 15 THz [57,58]. An additional Nosé-Hoover thermostat is applied on the electronic degrees of freedom with frequency 200 THz. Mechanical stresses are applied along the [001] (load) and [110] (shear) directions. The water molecules (12 per supercell) are initially positioned in the configuration that we have identified as the most stable between the carbon slabs, and then the shear stresses and normal pressure are gradually applied adopting the same computational scheme as described in Refs. [17,59].

3. Results

3.1. Tribologically-induced hydroxylation of the carbon film

We consider a sliding interface composed of a Si-incorporating C(001) surface partially hydrogenated and a fully hydrogenated H–C(001) countersurface. Si atoms are incorporated at substitutional dimer sites consistently with the experimental observation that silicon atoms in Si-DLC are surrounded by carbon atoms, and not by oxygen or other silicon atoms [61,62]. A density of Si atom corresponding to 8.3% is realized, which corresponds to a typical dopant concentration in Si-DLC [33,40,38,63]. Fig. 1 shows subsequent snapshots of the system dynamics under normal pressure of 5 GPa and shear stress of 1.25 GPa (the entire simulated trajectory is displayed in the movie of Supplemental data): after the onset of sliding, one of the substitutional Si atom captures a hydroxyl group from a confined water molecule, and a similar event happens immediately afterward at another Si-sites. OH adsorption occurs also at unsaturated C-sites, but with lower frequency. To clarify the effect of Si doping, we repeat the simulations maintaining the same tribological conditions and interfacial hydrogen coverage, but without the incorporation of any Si atom. Fig. 2 shows the number of adsorption events as a function of time for both the doped and undoped systems. The comparison of the results clearly indicates that the Si incorporation dramatically increases the reaction rate for water dissociative adsorption.

Supplementary video related to this article can be found at http://dx.doi.org/10.1016/j.carbon.2016.02.078.

To verify the robustness of the result, we repeat the sliding simulation for both the systems of Fig. 2, but with different shear stresses of 1.25 GPa, 0.88 GPa and 0.0 GPa. The different adsorbate terminations of the surface sites observed during the simulations are reported in Table 1. The result shows that the Si sites present a probability to adsorb hydroxyl groups five time higher than the C sites, indicating that the Si dopants function as catalytic sites for hydroxylation.

The acceleration of the hydroxylation reaction by Si dopants observed in the dynamic simulations is consistent with our previous study based on static *ab initio* calculations, which shows that the presence of Si dopants considerably decreases the energy barrier for water dissociation at the surface [45]. Moreover, the analysis of the electronic charge displacements revealed that the larger polarization of Si–OH bonds with respect to C–OH bonds due to electronegativity differences, stabilizes hydroxyl adsorption at Si sites, in agreement with the distribution of the reaction products