

氏名	わん やん 王 楊
研究科, 専攻の名称	東北大学大学院工学研究科 (博士課程) 機械機能創成専攻
学位論文題目	Molecular Dynamics Simulations on the Tribochemical Reactions of Diamond-like Carbon and Their Roles in the Friction and Wear Mechanisms (ダイヤモンドライクカーボンのトライボケミカル反応とそれらが摩擦・摩耗メカニズムに与える影響に関する分子動力学シミュレーション)
論文審査委員	主査 東北大学教授 足立 幸志 東北大学教授 徳増 崇 東北大学教授 久保 百司

論文内容要約

Achieving low friction of sliding materials is of particular importance for the industrial applications such as car engines, bearings, and hard-disks. Routinely, diamond-like carbon (DLC) which is an amorphous structure consisting of the sp^3 hybridized carbon atom in diamond, sp^2 hybridized carbon atom in graphite, and hydrogen atom, is widely used as a solid lubricant coating on the sliding material surfaces to reduce the friction because of its excellent tribological properties such as low friction, high hardness, and good chemical stability. Generally, various tribochemical reactions are coupled together at the friction interface, strongly affecting the lubricity of DLC. For further improving the lubricity of DLC, it is essential to elucidate the tribochemical reaction dynamics and their roles in the friction mechanisms of DLC. Molecular dynamics (MD) simulation approach is a widely employed tool to study the chemical reaction dynamics and atomic-scale friction processes which are hard to be clarified by conventional experiments. Although some of the tribochemical reactions of DLC are investigated previously by the first-principle calculations, comprehensive understandings of the reactions and friction mechanisms under various extreme conditions like stress and temperature are still required. For this purpose, in this doctoral thesis, the simulation technique for studying the tribochemical reactions of DLC under different conditions is developed based on the tight-binding quantum chemical molecular dynamics (TB-QCMD) method, to comprehensively reveal the tribochemical reactions and providing guidelines of reducing the friction.

On the other hand, although lubricity of DLC can be successfully improved via above investigations, wear of DLC does not only deteriorate its lubricity but also limit the improvement of the durability and reliability of DLC, leading to a strong demand of reducing the wear. To obtain the theoretical guideline of wear reduction, understanding the wear mechanisms of DLC are essential; however, for the investigations on the wear phenomenon by using MD simulations, the large-scale simulation is necessary while chemical reactions should be also handled during the MD simulations because the wear process involves a series of complicated bond formations and breakings. In this thesis, to make the study on wear process possible, the large-scale MD simulation technique is developed based on the reactive force field (ReaxFF), which is able to precisely deal with the bond formations and breakings with the size of tens of nanometers. Thus, by using the developed large-scale simulation technique, the wear mechanisms of DLC and the effects of hydrogen atoms on the wear are revealed, and furthermore, based on the obtained insights into the atomic-scale wear process, a theoretical wear law of quantitatively calculating the wear amount is established. Overall, this thesis contributes to the development of DLC as a theoretical guideline of reducing the friction and wear.

Chapter 1 Introduction

In this chapter, a general introduction of this doctoral thesis is given, demonstrating the background, current difficulties, and main objectives of this doctoral thesis.

Chapter 2 Methodology

Here the details of computational method are described, giving an overall scope on the MD simulations, TB-QCMD method, and ReaxFF potential.

Chapter 3 Tight-binding Quantum Chemical MD Study on the Tribochemical Reactions and Friction Mechanisms of DLC: Effect of Tensile Stress

Since the tensile stress generated at the DLC surfaces strongly affects the frictional behaviors, in this chapter, friction

simulation technique with the consideration of stress is developed on the basis of the TB-QCMD method to reveal the tribochemical reactions of DLC under the tensile stress and their effects on the friction process. The DLC without tensile stress shows the low friction coefficient of around 0.02; however, the tensile stress results in an obvious increase in the friction coefficient of DLC due to the formation of interfacial C-C bonds between two DLC substrates. Furthermore, the atomic-level wear of DLC is also observed under high tensile stress driven by the shear of friction interface when a lot of interfacial C-C bonds are formed. These atomic-level wear events are proposed to finally cause the macroscale wear of DLC in experiment.

Chapter 4 Tight-Binding Quantum Chemical MD Study on the Tribochemical Reactions and Friction Mechanisms of DLC: Effect of Temperature

DLC usually slides against alumina in various industrial applications such as sliding bearings. Experiments show that the temperature at the friction interface of DLC/alumina plays a particularly important role in the frictional behaviors; however the underlying mechanisms are still hidden by the complex tribochemical reactions. Thus, in this chapter, by developing the simulation technique with the consideration of temperature based on TB-QCMD method, the effect of temperature on the friction mechanism of DLC sliding against crystal alumina is revealed for the first time. With the temperature varying from 300 to 1000 K, three friction regimes are observed. At low temperatures of 300-600 K, smooth sliding behaviors between the DLC and alumina substrates are observed and low friction coefficients of around 0.05 are obtained. At 600-800 K, interfacial C-O and C-Al bonds between the DLC and alumina substrates are formed during friction, leading to an increase in the friction coefficient. At temperatures higher than 800 K, the graphitization of the DLC substrate is observed and a graphite-like surface is formed. The graphite-like surface of DLC suppresses the formation of interfacial C-O and C-Al bonds, leading to a decrease in the friction coefficient. The MD simulations of DLC/alumina reveal that the volcano-type temperature dependence of friction coefficients is due to the tribochemical reactions generating interfacial bonds at 600-800 K and the graphitization of DLC reducing the number of interfacial bonds at 800-1000 K. Overall, the simulations provide the atomic-scale insights into the tribochemical reactions and structural changes of DLC and their effects on the friction behavior.

Chapter 5 Development of ReaxFF Parameters for Hydrocarbon System Enabling Large-Scale MD Simulations of DLC

In order to investigate the wear mechanisms of DLC, in this chapter, the reliable reactive force field (ReaxFF) parameters for H/C system are successfully developed on the basis of the previous reported carbon parameters [*J. Phys. Chem. A* 2015, 119, 571-580], by training with the first-principles calculations. As a result, the developed H/C parameters in ReaxFF show very good agreements with the first-principles calculation results on the bond energies (H-H and H-C), angle energies (H-H-H, H-C-H, and H-C-C), van der Waals interactions between hydrogen atoms, and various reaction barriers.

Chapter 6 Classical MD Study with ReaxFF Potential on the Effects of Tribochemical Reactions and Wear Mechanisms of DLC

Wear not only leads to the failure of lubricity of DLC but also reduces its durability and reliability. To better use and improve DLC, understanding the wear mechanisms and then reducing the wear are strongly required. In this chapter, the large-scale simulation technique is developed on the basis of the reactive MD simulations with the developed high-accuracy ReaxFF parameters in Chapter 5, making the investigation on the wear mechanisms possible for the first time. Since the hydrogen atoms in DLC bulk are reported to strongly affect the wear behaviors of DLC, the models of hydrogenated DLC with various hydrogen concentrations are prepared and used to perform the wear simulations. Here, two major wear mechanisms of DLC are found: 1) adhesion-induced mechanical wear which indicates the transfer of carbon atoms to the counter sliding substrates and 2) atomic-scale chemical wear that is the generation of hydrocarbon molecules like methane, ethane, and ethylene emitting from DLC surfaces. Furthermore, it is interesting to find that the mechanical wear decreases while the chemical wear increases with increasing the hydrogen concentration in the DLC bulk, showing a change of the dominant wear mechanism of DLC as the hydrogen concentration increases. The decreasing mechanical wear is because the chemical adhesion of two sliding DLC surfaces is suppressed by increasing the hydrogen atoms in the bulk, while the increasing chemical wear originates in that carbon atoms in the DLC bulk are less bonded with each other as the hydrogen concentration increases making the hydrocarbons easily to emit from DLC surface during the friction. The total wear of hydrogenated DLC as a sum of both the mechanical and chemical wear shows a concave hydrogen concentration dependence with an optimal hydrogen concentration of around 20% for the wear reduction. This chapter gives a fundamental understanding of the wear mechanisms of DLC at the atomic scale for the first time, which demonstrates that the wear reduction of DLC should rely on the hydrogen concentration because the dominant wear mechanisms are different.

Chapter 7 Tribochemical Reactions of DLC in the Hydrogen Gas Environment and Their Effects on the Wear Reduction

For the purpose of reducing the wear, this chapter makes efforts to take the effects of environmental gases on the wear behaviors of DLC into consideration by using the developed wear simulation technique in Chapter 6. Here the effect of hydrogen gas environment on the wear behaviors of hydrogen-free DLC is focused. The wear behaviors of hydrogen-free DLC in the vacuum is same as that in Chapter 6. During the friction, gaseous hydrocarbon molecules are emitted from DLC surfaces, leading to a gradual depletion of surface hydrogen terminations and remaining a large number of high reactive sites like dangling bonds on the surface. These reactive sites form the interfacial C-C bonds, indicating a severe surface adhesion and resulting in a high adhesion-induced mechanical wear. However, in the hydrogen gas environment, hydrogen gas dissociatively adsorbs to DLC surfaces, replenishing the depleted hydrogen terminations and inhibiting the formation of interfacial C-C bonds. Due to the suppression of interfacial C-C bonds, the surface adhesion and adhesion-induced mechanical wear of DLC are also reduced comparing to that in the vacuum. This chapter demonstrates that the tribochemical reactions losing and replenishing surface hydrogen terminations accelerate and suppress the wear of DLC, respectively, giving a theoretical guideline to reduce the wear of DLC by controlling the environment.

Chapter 8 Development of a Robust and Applicable Wear Law Based on the Reaction Rate Theory

In Chapter 6 and 7, the wear mechanisms of DLC are qualitatively investigated by the large-scale reactive MD simulations. However, for the purpose of better designing the high wear-resistant DLC, a theoretical wear equation which quantitatively predicts the wear amount of DLC under different conditions is strongly needed. In this chapter, based on the atomic-scale wear process obtained in Chapter 6, an applicable theoretical wear law of DLC is developed by assuming the wear event as the chemical reactions containing following two steps: (a) surface atoms form the interfacial bonds due to the normal load (F_N) on real contact area (A_{real}) and then (b) these reacted surface atoms are partially desorbed from surfaces by the shearing of interfacial bonds finally leading to a wear. By applying reaction rate theory on the above two reactions, the theoretical expression of the wear amount (N_{wear}) can be deduced as $N_{wear} \propto \exp[k(F_N/A_{real})^2 - \Delta E_{tot}/k_B T] A_{real}$, where k is a calculable factor relating to temperature and material properties like elastic modulus, ΔE_{tot} is the summed energy barriers of the above two reactions, and k_B and T are Boltzmann constant and temperature, respectively. The above expression implies that the theoretical calculation of wear amount (N_{wear}) depends on the real contact area (A_{real}) which varies with different contact situations and contact scales. For the macroscale contact, the surface roughness leads to a linear relation of $A_{real} \propto F_N$, and thus, we have $N_{wear} \propto F_N$. However, for the nanoscale contact, since the contact mechanics for rough surfaces are failed, A_{real} does not scale with the F_N anymore. Next, to verify the applicability of proposed wear law, reactive MD simulations are performed and compared with the wear law by using the models of two different contact situations: (a) rough-surface contact and (b) smooth ball-on-disk contact. According to the continuum contact mechanics, rough-surface contact causes a linear relation of $A_{real} \propto F_N$ and ball-on-disk contact with smooth surfaces shows that $A_{real} \propto F_N^{2/3}$, representing the macro and nanoscale contact, respectively. For either A_{real} - F_N relation, the theoretically predicted N_{wear} should be able to fit the MD results by choosing proper ΔE_{tot} , and furthermore, the extracted values of ΔE_{tot} should be independent of contact situation because they only relate to the material type. As the results, the theoretically predicted N_{wear} for each contact fit with MD results very well while the extracted ΔE_{tot} are 0.3359 eV for rough-surface and 0.3351 eV for ball-on-disk. The extricated ΔE_{tot} for both contact models are almost the same, showing good applicability of the proposed wear law. Overall, this chapter demonstrates the fundamental theory on the wear, showing a very huge academic contribution.

Chapter 9 Final Conclusions

As a summarization, the present doctoral thesis reveals the tribochemical reactions under various friction conditions such as stress and temperature and their effects on the friction mechanisms of DLC (Chapter 3 and 4). Subsequently, by developing the high-accuracy ReaxFF parameters (Chapter 5), the wear mechanisms of DLC are clarified for the first time (Chapter 6 and 7) and furthermore the theoretical wear law quantitatively predicting the wear amount of DLC is developed (Chapter 8). This thesis contributes to the friction and wear reduction of DLC as a theoretical guideline.