Multi-Physics and Multi-Scale Simulations on Super-low Fricion Mechanism of Diamond-like Carbon

氏　　名	ばい　しゃん　だん 白　　珊　丹
研究科，専攻の名称	東北大学大学院工学研究科（博士課程）バイオロボティクス専攻
学 位 論 文 題 目	Multi-Physics and Multi-Scale Simulations on Super-low Friction Mechanism of Diamond-like Carbon （ダイヤモンドライクカーボンの超低摩擦機構に関するマルチフィジックス・マルチスケールシミュレーション）
論 文 審 査 委 員	主査　東北大学教授　久保　百司　東北大学教授　堀切川　一男 東北大学教授　足立　幸志

論文内容要約

Recently, in points of view on the economy and environment, the development of new low-friction technology is strongly required, because the friction is very severe problem for energy loss. Realization of low-friction technology is essential and indispensable towards the achievement of a low carbon emission society. Therefore, to understand the friction and wear behaviors at contact surfaces is very important for the development of the low-friction technology. Liquid lubricants are regularly employed to reduce the friction at contact surfaces in many mechanical systems, such as vehicles and industrial robots. On the other hand, solid lubricants have been recently used in precision mechanical equipment, such as microelectromechanical systems and aerospace instruments. Diamond-like carbon (DLC) has an amorphous carbon structure and contains both sp2 and sp3 carbon (Csp2 and Csp3) atoms, which is one of the most promising solid lubricants because of its low friction, low abrasion, hardness, and chemical resistant properties. DLC is widely applied to industries, such as aerospace instrument, automobile, magnetic disc and so on. However, tribological properties of DLC are unstable reported by Fontaine and co-workers. Recently, the doping and termination of DLC films with some elements and their influence on the structure change and tribological properties are paid attention. Moreover, influence of tribo-chemical reactions on tribological properties are investigated by the experimental analytical techniques. However, understanding the details of low friction mechanism and mechanical properties of doped and terminated DLC are difficult to be revealed only by the experimental technology. Furthermore, the low friction property of DLC in water lubrication is also unrevealed. Computational methods are very efficient technique to investigate the low friction mechanism and mechanical properties in details at atomic scale. In this study, we aim to clarify the tribo-chemical reaction of low friction mechanism and mechanical properties of modified DLC films under condition of ultra-high vacuum using multi-physics and multi-scale computational methods. The low friction mechanism of DLC in water lubrication is also investigated by the computational methods, which is expected for friendly environment. Furthermore, on the basis of the above knowledge, we intend to design new low-friction materials and systems. The contents of this thesis are following.

Chapter 1, General Introduction

Chapter 2, Computational Methods

Chapter 3, Influence of Hydrogen- and Fluorine-Termination on Friction Reduction Mechanism of Diamond-like Carbon Surfaces

Chapter 4, Investigation on Mechanical Properties of Hydrogenated and Fluorinated Diamond-like Carbon Films

Chapter 5, Effects of Contact Pressure on Low Friction Mechanism of Fluorine-terminated Diamond-like

Carbon Films

Chapter 6, Investigation on Tribo-Chemical Reaction of Diamond-like Carbon in Water Lubrication

Chapter 7, Generation of "Graphene Arch-Bridge" on Diamond Surface by Si-Doping

Chapter 8, General Conclusions

The details of this study are described in the following chapters.

Chapter 1, General Introduction

We give the general introduction and objective for this study. The purpose of this study is investigation on the low friction mechanism of solid films and evaluation of its mechanical properties. Furthermore, on the basis of the above knowledge, we intend to design new low-friction materials and systems. In this study, we perform the multi-physics and multi-scale simulation techniques. The low friction mechanism is investigated by molecular dynamics (MD) method, tight-binding quantum chemical molecular dynamics (TB-QCMD) method, and first-principles calculations. The mechanical properties are evaluated by the finite element method (FEM).

Chapter 2, Computational Methods

In order to clarify the low friction mechanism and mechanical properties of DLC, modified DLC films, and DLC in water lubrication at atomic scale, we use multi-physics and multi-scale computational methods. The details of MD method, TB-QCMD method, first-principles calculations, and FEM are described.

Chapter 3, Influence of Hydrogen- and Fluorine-Termination on Friction Reduction Mechanism of Diamond-like Carbon Surfaces

The friction properties of DLC film are improved by doping of F atoms, which is studied in experiment. However, the low friction mechanism of fluorinated DLC is not revealed. In this chapter, the friction reduction mechanism of DLC and hydrogen- and fluorine-terminated DLC (H- and F-terminated DLC) films are investigated using MD and tight-binding quantum chemical (TB-QC) calculations. Atomistic-scale friction dynamics of DLC, H- and F-terminated DLC models in which the unsaturated bonds on their surface are terminated with 100% H and F atoms are investigated by MD. The F-terminated DLC model shows lower friction than that of the H-terminated DLC model because of stronger repulsive Columbic force between F atoms at the surfaces. On the other hand, strong van der Waals interaction acting on the interface was observed for the H-terminated DLC model compared to that for the F-terminated DLC models. TB-QC calculation indicates the bond formation between the DLC surfaces, and the repulsive interaction is observed for H- and F-terminated DLC. Those interactions would make the difference in the friction properties among the studied models.

Chapter 4, Investigation on Mechanical Properties of Hydrogenated and Fluorinated Diamond-like Carbon Films

We clarify the low friction mechanism of H- and F-terminated DLC using MD and TB-QC calculations in chapter 3. Furthermore, investigation of their mechanical properties is also necessary. To evaluate their mechanical properties, we investigate the hydrogenated DLC models containing 10, 20, 30, and 40% H atoms and fluorinated DLC models containing 10, 20, 30, and 40% F atoms using FEM simulation. Their accurate Young's modulus and Poisson ratio are needed to describe the stress-strain relationship. For this purpose, the elastic modulus of the models is computed by MD method in which a strain is introduced uniaxially to the model and the stress along the same axis is analyzed. By this procedure, Young's modulus

and Poisson ratio for the hydrogenated and fluorinated DLC models are calculated and introduced to the FEM calculations as the parameters. The nanoindentation simulation is performed by FEM. In the simulation, the load is applied to the diamond indenter and increased from 0 to the maximum of 1000 □N. 160 nm of penetration depth is observed at the maximum load. Hardness of hydrogenated and fluorinated DLC models is calculated from the penetration depth. The hardness values of hydrogenated DLC are 24, 18, 11, and 7 GPa for 10, 20, 30, and 40 % H content models, respectively, and that of fluorinated DLC are 23, 16, 9, and 5 GPa for 10, 20, 30, and 40 % F content models, respectively. The results indicate that the hardness decreases by increasing the H or F content. Moreover, the hardness of hydrogenated DLC is higher than those of fluorinated DLC films at the same content of H and F. This is because the bonding energy densities of hydrogenated DLC models are higher than that of fluorinated DLC models. The results show that the hardness of F-DLC decreases with increasing F content.

Chapter 5, Effects of Contact Pressure on Low Friction Mechanism of Fluorine-terminated Diamond-like Carbon Films

Although the low friction mechanism of F-terminated DLC is investigated by MD calculation in chapter 3, the tribo-chemical reaction of low friction mechanism is difficult to be clarified by MD calculation, since electrons are not considered in the MD, and most chemical reactions are induced by electron transfer. In this chapter, the super-low friction mechanism of F-terminated DLC is investigated by our TB-QCMD code and compared with that of H-terminated DLC. According to experimental study, we model the F-terminated DLC consisting of 23% F and 57% H atoms and H-terminated DLC consisting of 80% H atoms at the DLC surface. Under a contact pressure of 1 GPa, F- and H-terminated DLC show smooth sliding and low friction coefficients of 0.07 and 0.04, respectively. An ion radius of fluorine is larger than that of hydrogen, which leads to larger asperity of the F-terminated DLC surface. Thus, the friction coefficient of F-terminated DLC is a little larger than that of H-terminated DLC. Furthermore, under a high contact pressure of 7 GPa, chemical reactions of bond formation and dissociation are observed at the friction interface in F- and H-terminated DLC. C-C bonds formation is observed more frequently in H-terminated DLC than that in F-terminated DLC. The lifetime of C-C bonds in H-terminated DLC is much longer than that in F-terminated DLC. H-terminated DLC shows high friction coefficient of 0.42 due to strong C-C bonds at the friction surface, while F-terminated DLC shows the low friction coefficient of 0.08. The strong repulsive interaction at the interface of F-terminated DLC due to the large negative charge and large ion size of fluorine keeps the distance between DLC films under a high contact pressure and prevents the strong C-C bond at the friction surface, which leads to the low friction properties of F-terminated DLC. We suggest that the friction properties of DLC films under a high contact pressure are improved by F termination.

Chapter 6, Investigation on Tribo-Chemical Reaction of Diamond-like Carbon in Water Lubrication

Water as the lubricant can improve the friction properties and reduce the emission of CO2. Furthermore, experimental researchers observed that DLC has low friction properties in the condition of water lubricant even under high pressure. The friction coefficient of the DLC films drastically changes under the water lubricant, since some tribo-chemical reactions occur during sliding. Understanding details of the chemical reaction are difficult to be revealed only by experimental analyses. To investigate the tribo-chemical reaction of DLC under water lubrication, we also perform sliding simulation using TB-QCMD code. At first, we apply a contact pressure of 0.5 GPa on the top layer of upper DLC substrate. The C-OH bond is formed between the water molecule and the upper DLC substrate, and then the surface is terminated by OH group. Under the condition of a contact pressure of 0.5 GPa, we only observed OH termination on the surface of DLC

during friction. To clarify the tribo-chemical reaction of DLC under high pressure, we perform the sliding simulation under a contact pressure of 5.0 GPa. The water molecule approaches to the upper DLC substrate, and then the C-OH bond is formed between the water molecules and upper DLC substrate. Furthermore, it is very interesting to see the O atom is adsorbed on the upper DLC substrate, and the C-O-C bond is generated. The results show that the pressure condition affects the chemical reaction of water molecules during the sliding simulation. The friction coefficients are 0.81 and 0.05 for DLC under contact pressures of 0.5 and 5 GPa, respectively. It indicates that friction coefficient decreases with increasing contact pressure. We suggest that this result is due to the structure change from Csp3 to Csp2 on the DLC surface.

Chapter 7, Generation of "Graphene Arch-Bridge" on Diamond Surface by Si-Doping: First-Principles Calculation

The silicon doped DLC (Si-DLC) films were investigated by several groups, because the tribological properties of DLC films can be improved by doping of silicon. It is experimentally suggested that the rich Csp2 on the Si-DLC surface leads to low friction. However, the details of generation of Csp2 on the Si-DLC are not revealed. In this chapter, we reveal the generation of "Graphene Arch-Bridge" on diamond(111) surface by Si-doping via first-principles calculation. "Graphene Arch-Bridge" is different from simple graphene structure, because both its ends are pinned on the diamond surface and it has interesting arched-type curved structure. Large stress is induced around the doped Si atom in the Si-doped diamond(111) because Si atom has larger atomic radius than C atom. Then, this large stress leads to the transition of six-membered C ring to five-membered C ring. Furthermore, the exclusive C atom generated by the above transition from six-membered C ring to five-membered C ring changes from Csp3 to Csp2 and this Csp2 generates "Graphene Arch-Bridge" on the diamond(111) surface. These results suggest that the generation of five-membered C ring by the stress due to the Si-doping is the reason why the "Graphene Arch-Bridge" is generated on the diamond(111) surface. Finally, we propose that "Graphene Arch-Bridge" is the origin of the experimentally-observed super-low friction properties of the Si-DLC. Furthermore, we also suggest that "Graphene Arch-Bridge" of the Si-DLC leads to the lower wear properties than non-doped DLC because its ends are pinned on the DLC surface.

Chapter 8, General Conclusions

The conclusion of each chapter is summarized in Chapter 8.