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Molecular simulations for complex boundary lubrication

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ABSTRACT – Molecular simulation approach for boundary lubrication is presented. We report two phenomena. The first topic is Friction Fade Out phenomena. Reax Force Field is used to treat the chemical reaction and friction dynamics between ZrO_2 and diamond like carbon. We found the first step reaction of the formation process of the growth of transfer layer. The second topic is the first step of the formation of organic monolayer. We found that the effect of base oil is important in this process, which is different from "chain matching" idea. Other simulation technique is also discussed briefly.

1. INTRODUCTION

Molecular Dynamics (MD) has its origin in 1950s, and application to the tribology started in 1990s. At the beginning of the history, since supercomputers and hand-maid code to run the simulations are needed, MD simulation was for the experts in Universities or in large institutes. Recently, due to the low price of computers and growing of open-source simulation software, molecular simulation approach for tribology is open not only for the experts but for all tribologists including experimental researchers. In this talk we show our recent MD results to study boundary lubrications, show a limitation of MDs, and our recent approach for novel simulation methods.

2. MOLECULAR DYNAMICS SIMULATION FOR LUBRICATION

MD are mainly used for biological system and material system. For the material system, Lammps [1] ("Large-scale Atomic/Molecular Massively Parallel Simulator"), the open-source software distributed by Sandia National Laboratories, and highly parallelized, is widely used. Since Lammps do not have graphical user interface, commercial application programs are available to draw lubricant molecules in order to make input files. Lammps run on both PC and supercomputers such as K computer.

The authors used this simulator for several systems. For solid lubricants, all-atom simulations for investigating ultra-low friction mechanism of graphene transfer films [2], reveals that "thermal escape motion" [3] of lamellar materials found by coarse-grain simulation is reproduced by all-atom MD. The "thermal escape motion" is the strongest candidate to explain the very low friction between graphene transfer film and the substrate. Since the transfer film have degree of freedom during the physical or chemical adsorption on the counter-surface, two faced surface are stabilized in commensurate state. Then the occurrence of very low friction between commensurate surfaces should be explained. The well-known mechanism of "super-lubricity" which occur between incommensurate surfaces, cannot explain the phenomena.

3. RECENT RESULTS FOR BOUNDARY LUBRICATION

3.1 Friction of ethanol confined between DLC and YSZ

For surface coating, the sliding friction between ZrO_2 and diamond like carbon (DLC) film including small amount of water and ethanol molecules between them, are studied. Chemical reaction is treated in classical MD by using Reax Force Field (ReaxFF) [4]. Hydrogen terminated DLC and non-terminated DLC are used. ZrO_2 surface is taken from a literature. During the sliding, transfer of ethanol molecules to ZrO_2 is found in both type of DLC, which is thought to be very beginning of the transfer film formation in the Friction Fade Out phenomena [5]. Fully hydrogenated DLC shows very low friction which drops to 10^{-4} when ZrO_2 slide on the surface. In the experiments, ZrO_2 are stabilized by Y atoms (YSZ). When sliding between YSZ and DLC including ethanol system (Figure 1), dissociation of ethanol molecules and chemical bonding to the solid surface are found. This means that YSZ is more reactive than ZrO_2.

Figure 2 shows the film thickness (number of ethanol molecules) dependence on ratio of chemical reaction. Chemical reaction shows peek in single layer system whereas chemical reaction decreases as the film thickness increases. This is because, since the chemical reaction is due to the friction energy, single layer shows solid like friction so that to react enough, on the other hand, multi-layered system shows low friction due to liquid lubrication like dynamics. In many tribological system, less lubricants sometime show effective for boundary film formation or polishing. We think our result show symbolic case of these phenomena.

3.2 Formation process of oiliness agents on metal surface

For boundary lubrication, formation process of organic acid molecules (palmitic acid) as additives in hydrocarbon base oil on the charged metal surface are studied using all-atom molecular dynamics [6]. After the relaxation process, the base oil molecules made highly oriented (laid) adsorbed layer on the surface at first. Then the additive molecules is prevented to physically adsorb

on the surface (Figure 1). The adsorbing time is due to the structure of base oil. When the base oil is linear (n-hexadecane), the adsorbing time is long, since the base oil form highly ordered layer. When the base oil is branched, the adsorbing time is shorter then linear oil. This is because the adsorbed layer structure of the base oil is random than a linear oil. This finding is novel solvent effect other than "chain matching" (Figure 2) [7]. "Chain matching" is the effect that when the chain length of the linear base oil and the additives are same, the boundary film become strong so that inhibit from pull off during the sliding. Therefore, this effect is, saying, effect for the breakage for the boundary film. Our finding of the adsorbing process is effect for the formation of the boundary film. This may be complement idea with chain matching for boundary lubrication of organic additives.

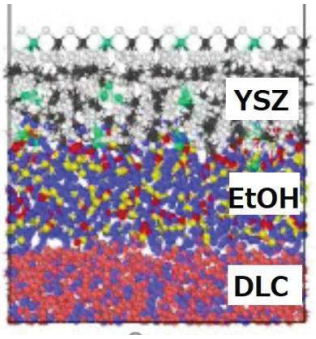

Figure 1 Molecular dynamics simulation of the friction of confined system between YSZ and DLC, and ethanol molecules. Chemical reaction is treated by Reax Force Field.

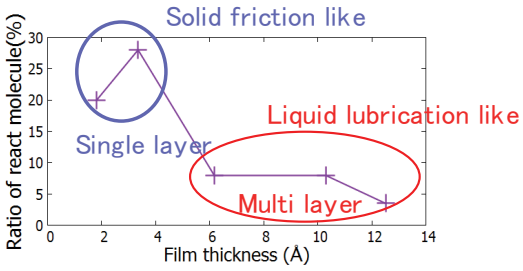

Figure 2 Ratio of chemical reaction of ethanol confined between YSZ and DLC.

3.3 Other system

We also analyzed the properties of Benzotriazole molecule, which is one of the anti-copper-corrosion additive, absorb onto copper surface by reaxFF molecular dynamics. This is reported in another presentation.

The limitation, however, are found easily if we consider about large system effect such as long-range Coulomb interactions [8], surface roughness, heat generation and transportation on the sliding surfaces. Our recent approaches using smoothed particle hydrodynamics (SPH) are also presented in this conference.

4. SUMMARY

The all-atom MD simulation is useful not only for simulating the molecular ensemble, but including chemical reactions. In the system of ethanol confined between DLC and YSZ system, ratio of the chemical reaction decreases with the increase of the film thickness, which is first report of this kind of "Tribo Chemical Reaction". For the oiliness agen t system, we found layered structure of the base oil is bottle neck of adsorbed layer formation, which is different than the concept of "chain matching".

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