

Tribochemical mechanism of superlubricity of phosphoric acid: a reactive molecular dynamics study

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1. Introduction

The achievement of further reduction or even elimination of friction, i.e. the so-called superlubricity [1], is a challenging goal of human beings. In the past decade, there were a few studies on superlubricity mechanism, some focus on the tribochemical reactions [2-4]. In this context, one should expect the phase transition or tribochemical products would lead to an interfacial structure with low shear strength. In a recent remarkable experimental effort made by Li et al., a silica/phosphoric acid (PA) system was examined [5]. Noticeably, there was significant tribochemical reaction in the running-in period, during which the friction coefficient decreased drastically to below 0.01, and a gel-like film was formed on the surface. This phenomenon indicates that the tribochemical reaction plays an important role in this superlubricity system. Shedding light on this system from atomistic scale would thus greatly assist building up a tribochemical theory of superlubricity. For this reason, in the present study, a state of PA superlubricity is simulated by reactive molecular dynamics where the extremely low friction (COF=0.02) is achieved by water molecules generation with tribochemical reaction.

2. Methods and Results

The MD simulation was performed with the LAMMPS code [6], and the forces between atoms are derived from ReaxFF, a new general bond-order-dependent force field based on extensive ab initio calculations, which was developed by van Duin and Goddard [7]. For the simulation, a sliding couple model for friction simulation was constructed by bringing two passivated quartz models into a face to face structure, afterwards, inserting a few phosphoric acid molecules randomly. The top layer of the upper substrate was forced sliding with a constant velocity of 100 m/s with an external normal pressure of 600 MPa.

It is observed that the friction force decrease drastically during the first 300 ps, accompanied with structure changes in lubricant, as shown in Figure 1. Inset (a) shows that, in the first decreasing step, the lubricant is divided into two layers due to confinement and each phosphoric acid still keeps as a single molecule. However, inset (b) shows that, after 1.2 ns phosphoric acid does not keep as single molecules any more, but connect to others with chemical bonds to form a polymer-like structure, along with the generation of a large amount of water molecules, depicted by blue colors in inset (b). Obviously, it is the tribochemical

reaction that leads to the aforementioned structure changes. Meanwhile, we find from the snapshots that the lubricant movement begins to exhibit some ordering that the atoms of lubricant move as a whole, which indicates a solidification transition of the lubricant. In previous perspective of friction reduction, this solidification transition is undesirable: because of the increasing chemical connectivity and thereby the promoting lateral shear stiffness of the whole lubricant. However, in the present work, along with the solidification transition, the friction coefficient keeps decreasing. That suggests the existence of a novel lubrication mechanism induced by tribochemical reaction. We find that it is the water molecules generated by the tribochemical reaction that act as a highly efficient lubricant, whose quantity and distribution is the matter of great account.

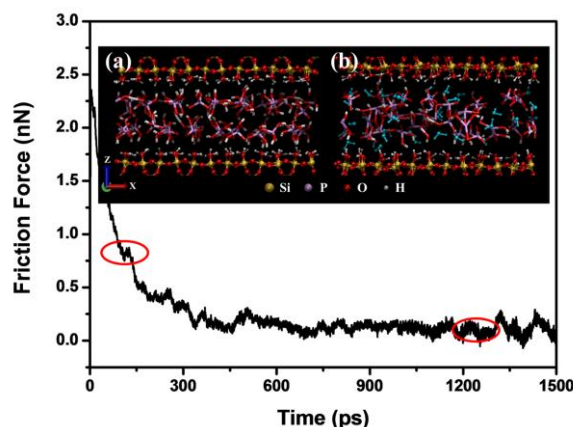


Fig.1 Time evolution of friction force. Snapshots of lubricant structure: (a) in the first decreasing step; (b) in the last step.

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3. References

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