Ab initio investigation of tribochemical processes at diamond and iron interfaces

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1. Introduction

Tribologically-induced chemical modifications of surfaces interacting with lubricants or other molecules present in the environment surrounding the sliding media can substantially change the tribological performances of the materials in contact, therefore it is highly desirable to understand how they take place at the microscopic level. However, tribochemical reactions are difficult to be monitored in real-time, which leaves a gap in the atomistic understanding required for their control.

We apply *ab initio* calculations to atomistically describe tribochemical processes that modify the surface termination and elucidate their effects on interfacial adhesion and friction. We consider the cases of diamond and iron interfaces.

2. Load-induced confinement activates diamond lubrication by water

We report the real-time atomistic description of the tribochemical reactions occurring at the interface between two diamond films in relative motion, by means of large scale *ab initio* molecular dynamics. We show that the load-induced confinement is able to catalyze diamond passivation by water dissociative adsorption. Such passivation decreases the energy of the contacting surfaces and increases their electronic repulsion. At sufficiently high coverages, the latter prevents surface sealing and, thus, lower friction as observed by experiments.[1, 2]

Our simulations show that the tribological conditions alter the surface kinetics and thermodynamics. In particular, we demonstrate that confinement under pressure is the driving force for molecular dissociation and reaction rates are functions of load. [3]

3. Dissociative adsorption of trimethyl phosphite at the Fe(110) surface. Effects of phosphorous and sulfur on adhesion and shear strength of iron surfaces.

Gas phase lubrication experiments revealed the trimethyl phospite (TMPi) effectively reduces friction at steel interfaces thanks to the tribologically-induced formation of iron-phosphide. To get atomistic insight into this issue, we study the mechanisms of iron phosphide formation from the dissociative adsorption of trimethyl phosphite (TMPi) at the Fe(110) surface. We identify the reaction paths for P release on the surface by means of the nudged elastic band method and discuss the effects of extra oxygen to account for the different tribological behavior observed for trimethyl phosphate (TMPa).[4]

We perform a comparative study on the effects of phosphorus and sulfur in reducing the adhesion and shear strength at iron interfaces. The results reveal important differences on the tribological effects of the two different interfacial species.

4. Summary

We apply *ab initio* calculations to investigate tribochemical processes at diamond and iron interfaces. We identify the microscopic mechanisms of surface passivation by dissociative adsorption of water and organo-phosphorous compounds, respectively. We investigate the effects of tribological conditions on reaction rates and surface thermodynamics. Finally we elucidate the functionality of the considered surface chemical modifications in reducing the interfacial adhesion and resistance to sliding.

5. References

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