7th World Tribology Congress, WTC 2022
July 10-15, 2022, Lyon, France

Reaction barriers for shear-driven tribofilm formation obtained from reactive molecular dynamics simulations

Stefan J. Eder[1,2)*], Nicole Dörr[1)], Karen Mohammadtabar[3)], Ashlie Martini[3)]

[1)]AC2T research GmbH, Austria
[2)]Institute for Engineering Design and Product Development, TU Wien, Austria
[3)]Department of Mechanical Engineering, University of California Merced, United States
*Corresponding author: stefan.eder@ac2t.at

In this study, we use reactive molecular dynamics simulations to study the reaction between di-*tert*-butyl disulfide, an industrially used extreme pressure additive, and a Fe (100) surface subjected to a range of temperature and pressure conditions. The reaction is analyzed in the context of the classic and extended Bell models. Our results show that the second-order extended Bell model can characterize the reaction more accurately than the linear classic Bell model.

Keywords: reactive MD, tribofilm formation, reaction barrier, extended Bell model

1. Introduction

Tribofilms protect the surface of mechanical components by reducing friction and wear, resulting in better efficiency and increased life time. These films are formed as a result of reactions between lubricant additives and surface components. The performance of these additives can be determined by the rate at which film-forming reactions happen. Shear stress is known to increase the rate of these tribochemical reactions, but the mechanism that causes this change in rate is poorly understood.

2. Methods

Our reactive molecular dynamics (MD) simulations were performed using the open-source code LAMMPS with the user-package reax/c implementation of the ReaxFF force field. The model system consists of 54 di-*tert*-butyl disulfide molecules confined between two Fe (100) slabs. Production simulations consisted of three stages – heat, load, and shear – each lasting 2 ns. In the heating stage, the model was subjected only to heat at constant temperatures ranging from 500 K to 700 K. A constant normal load was then applied to the rigid part of the top iron slab leading to pressures ranging from 0.25 GPa to 3 GPa. Finally, during the shearing stage, the top and the bottom iron slabs were moved in opposite lateral directions at ±5 m/s, respectively. A time-resolved bond-order analysis allows us to extract statistical data about the chemical reactions occurring in the system during the three stages.

3. Results and Discussion

The first step to making predictions about the formation of a sulfuric tribofilm is the identification of the rate-limiting reaction, which is the breaking of the S–C bonds [1]. Once this has been determined, the logarithm of the reaction yield can be plotted as a function of inverse temperature for the heat and shear stages of the simulation. When fitting these data to the classic (linear) Bell model, the slope of the fit constitutes the height of the reaction energy barrier, yielding different energy barriers for systems that were only heated and those that were also sheared [2]. In addition, 2D maps can be produced that allow lubrication and additive engineers to optimize their process parameters for fastest tribofilm generation, see Fig. 1. Finally, the functional form of the extended Bell model, which takes into consideration the non-linear effects of energetic curvature at the initial and the transition points of the key reaction, can provide a better fit to our data than the linear Bell model. This can be explained by a change in compliance as a response to the shear force acting on the molecule [3].

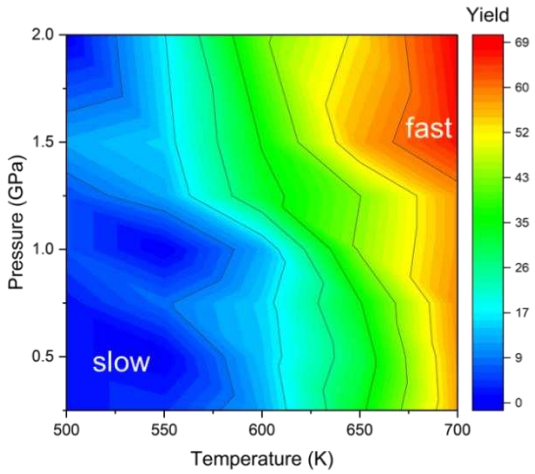

Figure 1: A pressure and temperature dependent reaction yield map gives an overview which parameter combinations lead to the fastest tribofilm formation.

4. Acknowledgments

This work was funded by the Austrian COMET-Program (project K2 InTribology1, no. 872176) and carried out at the "Excellence Centre of Tribology" (AC2T research GmbH).

5. References

[1] Mohammadtabar, K. et al., "Reactive molecular dynamics simulations of thermal film growth from di-tert-butyl disulfide on an Fe (100) surface," Langmuir, 34, 15681-15688, 2018.
[2] Mohammadtabar, K. et al., "Heat-, Load-, and Shear-Driven Reactions of Di-Tert-Butyl Disulfide on Fe (100)," The Journal of Physical Chemistry C, 123, 19688-19692, 2019.
[3] Mohammadtabar, K. et al.: "Second-Order Effects on Mechanically Driven Chemical Reactions: Shear-Driven Dissociation of Organosulfur Compounds on Iron. Journal tbd., 2020.