1 Introduction

The flow over hypersonic vehicles is characterized by extreme conditions with shock layer temperatures reaching 100,000 K and heat fluxes as high as 5 kW/cm². Thermal protection systems (TPS) consisting of carbon-based surface-ablating materials are effective structures that enable much of the heat flux to be carried away from the vehicle by the ablating material.

At these high temperatures, dissociated oxygen atoms (O) strike the TPS surface leading to several possible gas-surface chemical reactions. Specifically, the oxygen atom could chemically bond to the surface, it could recombine with another absorbed oxygen and leave the surface as a molecule (O₂), or the impinging atom could ‘oxidize’ the carbon surface resulting in products such as CO and CO₂ leaving the surface and being injected into the boundary layer. Such oxidation reactions result in the recession of the surface (surface ablation). Currently, much uncertainty exists in both the dominant reactions themselves as well as the rates of these reactions. The mechanisms and rates are required as part into state-of-the-art CFD simulations of hypersonic flows. Experimental determination of the chemical mechanisms themselves under extreme hypersonic conditions is difficult and often not easily inferred from macroscopic observations such as heat flux and surface recession measurements. However, this lack of computational chemistry continues to surface in step with advances in computational power, fundamental chemical studies may be able to provide insight into the chemical mechanisms and associated rates for such surface ablation processes.

The goal of this work is to develop finite rate models through large scale Molecular Dynamics (MD) simulations using the ReaxFF force field. Our current effort is to validate our ReaxFF simulations with existing data available from molecular beam experiments.

2 Molecular Dynamics Simulations

In contrast to previous computational chemistry work in this area where isolated single-ions collisions are studied on graphene sheets (one atomic layer), we simulate sequential gas-surface collisions on multi-layered graphene representing HOPG with large surface area. We do this to simulate the evolution of oxidized HOPG. The simulations are performed experimentally including the net removal of surface carbon atoms, the product species created, and the geometry of each ejected atom. Molecular Dynamics simulations are performed with the LAMMPS molecular dynamics program, using the ReaxFF potential.

2.1 ReaxFF Potential

ReaxFF is a bond order dependent potential that uses a relationship between bond distance and bond order along with bond order and bond energy to describe bond dissociation properly. This allows natural creation and destruction of bonds which is critical to our oxidation simulations. The complete energy of a system is given by a number with bond order and bond energy to describe bond dissociation properly. This allows natural creation and destruction of bonds. The complete energy of a system is given by a number with bond order and bond energy to describe bond dissociation properly. This allows natural creation and destruction of bonds which is critical to our oxidation simulations. The complete energy of a system is given by a number with bond order and bond energy to describe bond dissociation properly. This allows natural creation and destruction of bonds which is critical to our oxidation simulations.

The force field parameters used in the present simulations have already been optimized by Chenoweth et al. [1], and it has been demonstrated that graphene-oxygen interactions are accurately modeled with this potential.

2.2 Surface Preparation

The collision of a 5 eV O atom with the atomistic-scale HOPG surfaces in each MD simulation results in a significant increase in the temperature of the simulated ‘slab’ of HOPG. Under low pressure experimental conditions, any transfer of energy to the surface would be conducted into the bulk material. Therefore, in our simulations we thermostat the bottom layer of the HOPG slab to maintain a constant surface temperature. However, in addition, we also had to wait roughly 2.5 ps before the increased temperature of the top layer cooled back to the thermostated surface temperature as shown in Fig. 2. If the next gas-phase atom is injected prior to this, it hits a surface at an artificially high temperature, not representative of surface temperature. Therefore, our simulations predict this ratio of products to be roughly 1.4. The fact that our simulations predict more CO production than CO₂ and in a reasonable proportion compared to experiment is encouraging.

2.3 Surface Coverage

It is well known that pristine HOPG does not undergo oxidation due to O atoms colliding with large surface area. We do this to simulate the evolution of oxidized HOPG as observed from molecular beam experiments. In this work, we simulate the collision of hyperthermal (5eV) O atoms with Highly Oriented Pyrolitic Graphite (HOPG) and compare our results to the molecular beam experiments performed by Minton and co-workers.

2.4 Continuous Collisions

Oxygen atoms at 5eV are continuously injected towards the HOPG surface. A total of 1000 continuous collisions were performed. The simulation predicts the pit growth in the interplanar direction to be much more rapid than in the intraplanar direction. This was observed experimentally [3]. The surface temperature was maintained at 373K. In another set of experiments performed at 525 K, the experimental data predict the ratio of CO to CO₂ products as 1.2 while our simulations predict this ratio of products to be roughly 1.4. The fact that our simulations predict more CO production than CO₂ and in a reasonable proportion compared to experiment is encouraging.

3 Conclusions and Future Work

In this work, we have studied the oxidation of HOPG by hyperthermal O atoms. To avoid long wait times between successive collisions, we thermostated the system to the desired target temperature. It was also observed that the pristine HOPG sheet does not undergo oxidation even at temperatures of 1000 K. However, a surface covered with oxygen groups and small intrinsic defects lead to oxidation of the surface. We created a surface coverage of O atoms on the surface by allowing the O atoms to bond naturally to the surface instead of placing them in epitaxial form which resulted in flaking of the surface. Our continuous collision results are compared with the trends observed in molecular beam experiments. We observed that oxidation in the interplanar direction is faster than in the intraplanar direction as observed in experiments, and also that the oxidation rate increases with surface temperature. Finally, our simulations predicted higher production of CO₂ compared to CO and in relative amounts that were in agreement with experimental observations. These preliminary results are promising for the validation of our simulation techniques including the atomistic potentials and modeling assumptions.

In future work, we wish to characterize the rates quantitatively of all species formed on the surface and to make large time scales and scale MD simulations to validate our results as close as possible to available experimental data. We could then run simulations at high surface temperatures and study the crystal orientations to ascertain oxidation reactions present under hypersonic conditions for more realistic carbon-based surface ablating materials.

4 References