ARL-TR-9474 ● JUNE 2022

DEVCOM ARMY RESEARCH LABORATORY

Molecular Dynamics Analysis and Optimization of Ultra-High-Temperature Ceramic (UHTC) Compositions for Propulsion

by Robert Slapikas, Anindya Ghoshal, Luis Bravo, Muthuvel Murugan, and Douglas Wolfe

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED (From - To)
June 2022	Technical Report	June–December 2021

4. TITLE AND SUBTITLE
Molecular Dynamics Analysis and Optimization of Ultra-High-Temperature Ceramic (UHTC) Compositions for Propulsion

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Robert Slapikas, Anindya Ghoshal, Luis Bravo, Muthuvel Murugan, and Douglas Wolfe

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
DEVCOM Army Research Laboratory
ATTN: FCDD-RLW-VA
Aberdeen Proving Ground, MD 21005

8. PERFORMING ORGANIZATION REPORT NUMBER
ARL-TR-9474

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release: distribution unlimited.

13. SUPPLEMENTARY NOTES
ORCID ID(s): Ghoshal, 0000-0001-6338-1224; Bravo, 0000-0003-1604-9303; Murugan, 0000-0002-8314-3650

14. ABSTRACT
In this project, atomistic simulations were performed to analyze the material properties of ultra-high-temperature ceramics (UHTCs) for their use in aero-propulsion. Through mechanical testing and the use of the Green–Kubo formulation, the mechanical and thermal properties of transition metal borides ZrB_2 and HfB_2 are obtained using the classical molecular dynamics simulations code LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) and the bond-order Tersoff potential. These results show how the material properties of the UHTCs change with increasing temperature. The surface oxidization of single-crystal and polycrystalline silicon carbide is determined using the ReaxFF reactive interatomic potential. The simulations in this work were performed in the temperature range of 26–2000 °C. The findings from this work evaluate the influence of extreme environments and the volatilization of molecules from the UHTC surface due to oxidization; however, further analysis of the oxidization of UHTCs would need the use of newly parameterized reactive potentials.

15. SUBJECT TERMS
ultra-high-temperature ceramics, oxidation, molecular dynamics, high enthalpy, high-speed aerodynamics, Mechanical Sciences, Sciences of Extreme Materials, Weapons Science

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Anindya Ghoshal
Unclassified	Unclassified	Unclassified	UU	18	19b. TELEPHONE NUMBER (Include area code) 410-278-7358

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Acknowledgments

This project was financed by DEVCOM ARL, the DOD High-Performance Computing Modernization Program, and the High-Performance Computing Internship Program. Robert Slapikas would like to thank his DEVCOM ARL mentors, Drs Ghoshal, Murugan, and Bravo, for their mentorship and support throughout the project. He would also like to thank Dr Douglas Wolfe for guidance in making the simulations more experimentally accurate; and the Navy DOD Supercomputing Resource Center for the use of the Narwhal supercomputer where these calculations were performed.

Impact of Summer Research Experience

Robert Slapikas

I am currently a fourth-year PhD student in the Materials Science and Engineering department at The Pennsylvania State University. Previously I earned my MS in Materials Science and Engineering from the University of Florida and my BS in Mechanical Engineering from the Florida State University. While working toward my master's degree, I performed molecular dynamics (MD) simulations to study single-layered MoS_2 growth during high-temperature quenching. In this project, I studied and solved the issue of the "force stiffening" effect in a reactive empirical bond-order interatomic potential, which is an artifact caused by using a particular mathematical formula in the original interatomic potential. During my PhD research, I have been working on reducing the amount of wall time needed to run reactive MD simulations through optimization of simulation input parameters in the LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) code. Currently, I have been working to further the understanding of solid-solution interfaces through MD simulations to aid in designing and increasing the stability of catalytic materials.

I decided to apply for the DOD High-Performance Computing (HPC) internship program because the research project aligned with my interest in the oxidization and stability of materials through computational analysis, and I believed this experience could help facilitate my knowledge in this scientific field. The experience provided by the High-Performance Computing Internship Program and DEVCOM ARL has been extremely rewarding; I have been able to improve on the creation of my computational models to better describe the experimental conditions of ultra-high-temperature ceramics (UHTCs). I am extremely grateful for the opportunity to participate in this research project and to continue working with this project over the next year. This project has allowed me to not only learn more about the oxidization of UHTCs, but also improve my computer skills and develop the atomistic models used. Through this internship, I have created new research connections, and new opportunities have allowed me to further my academic and professional research career.

1. Introduction

Ultra-high-temperature ceramics (UHTCs) are materials of prominent interest in the field of aero-propulsion because of their high melting temperatures, high thermal conductivities, low thermal expansions, and good oxidation resistance.[1–4] These properties make them desirable candidates for materials in gas turbine engines and hypersonic applications. With the demand for future military engines to perform at temperatures above 2000 °C to improve their efficiency and power, transition metal carbides and borides are suitable materials for these applications.[3] Improvements in these material properties are also possible through the inclusion of silicon carbide (SiC) to produce UHTC composites.[2,3,5,6] However, there is a caveat—the reactions at the material surfaces have parabolic kinetics at high temperatures and are generally different than the reactions that occur at low temperatures, and the bottleneck in the development and advancement of these materials for aero-propulsion is their propensity to oxidize at the high temperatures of operation.[3,7] Some of these systems even observe completely new kinetic processes that are caused by the high thermal energy being applied to the system where chemical reactions are able to jump extreme energy barriers.[4,5,7] This has been especially prevalent in composite systems where there is a mixture of ionic and covalent bonding, whereas at low operating temperatures, these systems are mainly nonreactive. It is proposed that the oxidization of these materials is dependent on the physical chemistry at the oxidation site and the transportation of the reactants to this site.[1,6,7] Therefore, the aim of this project is to improve the understanding of the thermal and mechanical properties of the UHTC single crystals and composites and to provide an atomic-level understanding of the processes involved in the oxidation of UHTC composites. This will be performed by evaluating how UHTCs fail in extreme environments to enhance the performance and lengthen the lifetime of UHTCs.

2. Materials and Methods

To study the atomic interactions of UHTCs, classical molecular dynamics (MD) simulations are carried out using the open-source Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) code produced by Sandia National Laboratories.[8] To determine the mechanical and thermal properties of the UHTC ZrB_2 and HfB_2, the Tersoff potential is used, which is a three-body interaction potential that includes the effects of bond angles in the potential energy calculations.[9,10] These UHTC systems' mechanical properties were tested at 1600, 1800, and 2000 °C to bring the system to thermodynamic equilibrium using the Nosé–Hoover thermostat (NVT) ensemble using the NVT for temperature control

and timestep of 1 (fs). The thermal conductivity of the UHTCs is determined using the Green–Kubo formalism outlined by Eq. 1.[11] Through this equation, the lattice thermal conductivity (κ) of a material is correlated to a time average of the heat flux (J) in a particular direction, where V is the volume of the simulation, T is the temperature of the system, and k_b is the Boltzmann's constant.

$$k_{ij} = \frac{V}{k_b T^2} \int_0^\infty \langle J_i(0) J_i(t) \rangle dt \quad (1)$$

A reactive interatomic potential that includes charge transfer is needed to perform and understand the oxidation reactions of the UHTCs using MD.[12] However, all the desired UHTC systems are not parameterized. Therefore, the oxidization of SiC is determined using the reactive force field (ReaxFF), reactive interatomic potential, and charge equilibration.[12] In these simulations, single-crystal and polycrystalline materials were subjected to oxidization at high temperatures and pressures. These environments were simulated with a Langevin thermostat to regulate the temperature and a timestep of 0.25 (fs).

3. Results

3.1 ZrB_2 and HfB_2

In this work, MD simulations were performed to validate the interatomic potentials for ZrB_2 and HfB_2 at elevated temperatures. In these simulations, the thermal and mechanical properties of single crystals were calculated and considered to be reasonable in correlation with the literature.[7,8,10,13] In Table 1, the bulk, shear, and elastic constants are shown. The thermal conductivity of the ZrB_2 and HfB_2 was also determined. However, since both ZrB_2 and HfB_2 are anisotropic and have layered bonding between the transition metal and the boride, the thermal conductivity of the materials is different in the in-plane and out-of-plane directions.[11,14,15] Therefore, Green–Kubo simulations were performed to calculate the thermal conductivity in the two directions. It is known that both electronic and photonic contributions affect the total thermal conductivity of both these borides. However, using the Tersoff potential, only the contributions due to phonons can be determined.[15] In Figs. 1 and 2, the out-of-plane and in-plane thermal conductivities are graphed, respectively, as a function of temperature, where ZrB_2 thermal conductivity decreases at a faster rate than HfB_2 as temperature increases for both the in-plane and out-of-plane directions.

Table 1 Single-crystalline ZrB_2 and HfB_2 material properties calculated using MD

Material	Temp. (°C)	C11 (GPa)	C12 (GPa)	C13 (GPa)	C33 (GPa)	C44 (GPa)	B (GPa)	G (GPa)
ZrB_2	1600	246	107.3	289.3	1012.4	214.9	334.9	177.5
ZrB_2	1800	309.6	155.4	350.3	1044.7	190.8	379.7	150.2
ZrB_2	2000	329.6	155.6	416.3	870.9	175.2	366	139
HfB_2	1600	274.6	160.2	181.5	322.9	144.9	216.4	117.8
HfB_2	1800	254.7	118.3	175.7	327.4	140.9	202.3	119.7
HfB_2	2000	272.2	123.2	139.6	308.6	133.6	174.2	116.0

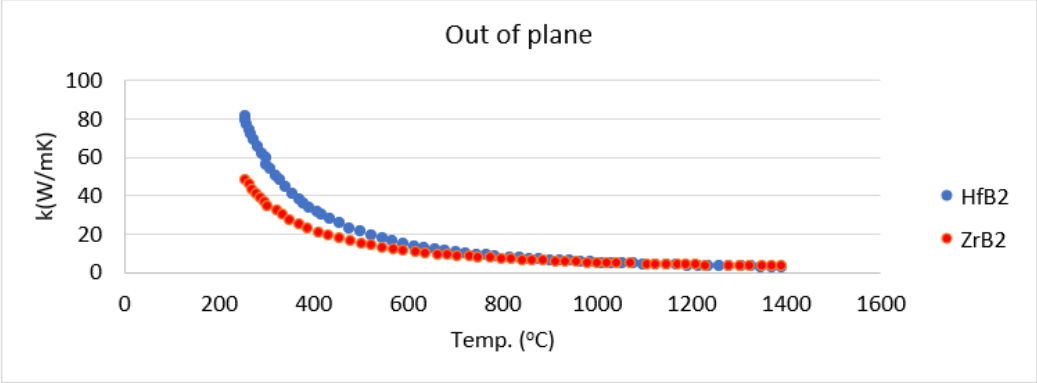

Fig. 1 Out-of-plane thermal conductivity as a function of temperature for single-crystal ZrB_2 and HfB_2

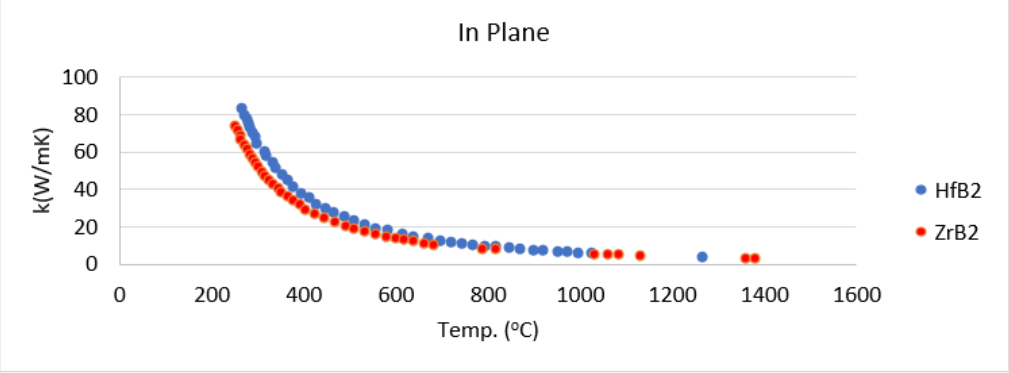

Fig. 2 In-plane thermal conductivity as a function of temperature for single-crystal ZrB_2 and HfB_2

3.2 Oxidization of SiC

Through classical MD simulations, the oxidization of α-SiC was observed for single-crystalline and polycrystalline structures. In the single-crystal α-SiC, surface oxidation was observed for a range of temperatures (26, 726, 1226, 1526, and 1726 °C) and a range of pressures (3, 6, 15, and 30 bar). The analysis of the crystal structures and oxide formation was done via predominant neighbor analysis using the visualization code OVITO.[16] An illustration of the oxidization of the single-crystal α-SiC is shown in Fig. 3. This simulation shows the creation of an active oxide film as oxygen atoms are injected into the surface at a velocity of Mach 10. As the pressure and temperature were increased, more of the SiC surface became oxidized.

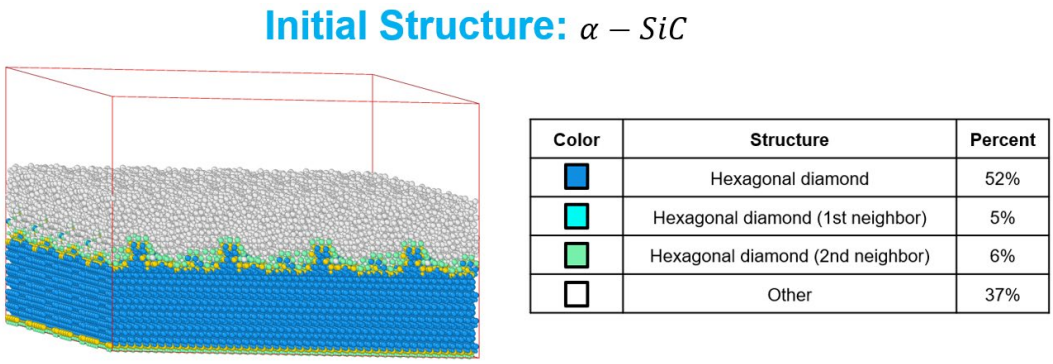

Fig. 3 Image of single-crystal α-SiC oxidized at a temperature of 1726 °C and a pressure of 30 bar. The white atoms labeled as "other" are considered disordered α-SiC or a disordered oxide; the table on the right illustrates the percentage of how much of the single-crystal α-SiC oxidized compared to the amount that is described as bulk and surface α-SiC.

In the oxidization of the polycrystalline α-SiC, the grain boundaries and the unordered SiC surfaces oxidized first, and then the oxidization of the α-SiC grains occurred as shown in Fig. 4, where the oxygen atoms start to form silicon oxide (SiO) in the regions where the crystal structure atoms are colored white. Through these simulations, we were also able to observe the volatilization of CO_2, CO, C_2O_2, and SiO_3 molecules from the surface of the polycrystalline α-SiC, as illustrated in Fig. 5. With these simulations, further analysis of the oxidization of UHTCs can be performed to understand the unique parabolic reaction kinetics in these extreme environments.[2,3,7]

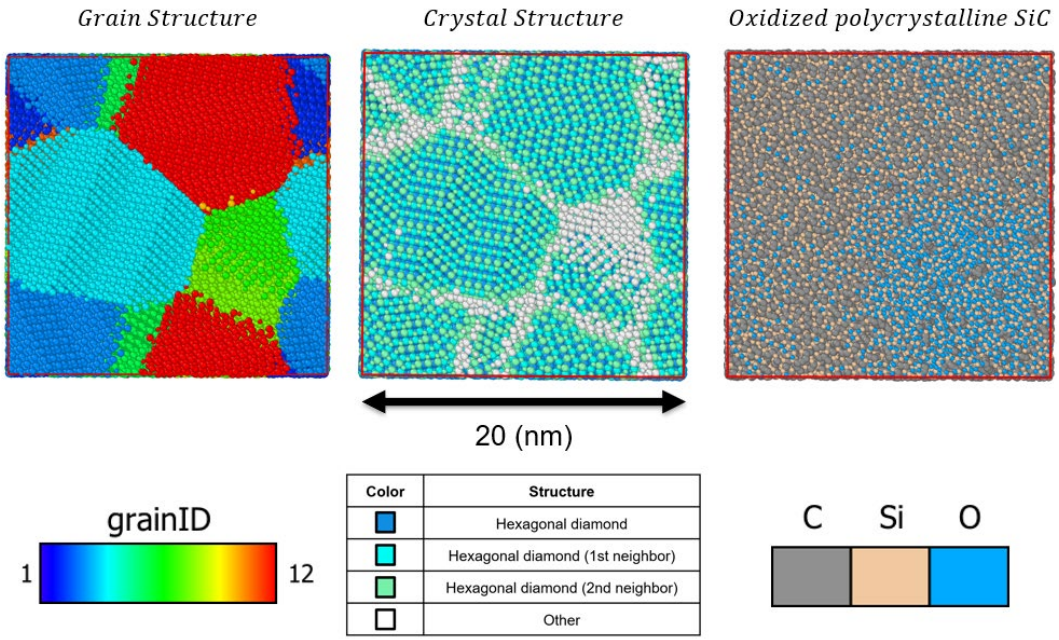

Fig. 4 Oxidixation of polycrystalline α-SiC: the polycrystalline α-SiC shows a top-down image. (Left) a depiction of the polycrystalline α-SiC showing the atoms colored by the individual grainID; (center) the same polycrystalline α-SiC where the atoms are colored by the crystal structure of the α-SiC, where the white atoms labeled as "other" are considered disordered SiC; (right) the polycrystalline α-SiC once it has been oxidized at a temperature of 1726 °C and a pressure of 30 bar.

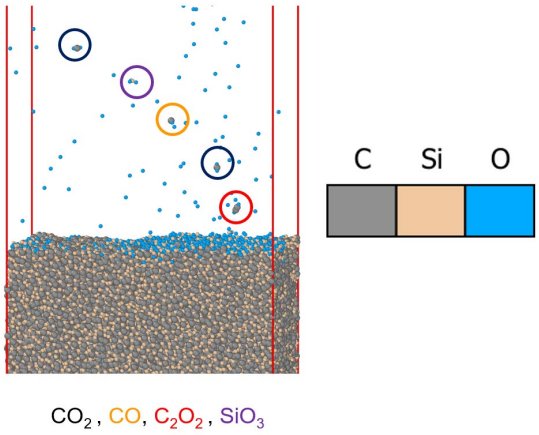

Fig. 5 Oxidixation of polycrystalline α-SiC where it is possible to see the formation of CO_2, CO, C_2O_2, and SiO_3 molecules. It is outlined by the corresponding color of the molecules and the corresponding colored circles. The simulation is performed at a temperature of 1726 °C and a pressure of 30 bar.

4. Conclusions

The Tersoff potential was used to predict the mechanical and thermal properties of single-crystal ZrB_2 and HfB_2. However, due to this potential not including charge transfer, further parameterization is needed to understand the oxide reactions with these UHTCs. Using the reactive ReaxFF interatomic potential, the prediction of single-crystalline and polycrystalline α-SiC at extreme environments was performed with the determination of the formation of surface oxides and the volatilization of CO_2, CO, C_2O_2, and SiO_3 molecules from the polycrystalline surface.

Future work will study the oxidization of the other transition metal carbides and borides. However, before oxide simulations can be performed, parameterization of the ReaxFF interatomic potential must be done for the rest of the elements in the desired systems. This requires performing density functional theory calculations to validate new structures for the systems. These calculations will include volume/energy equations of state, heats of formation, surface energies, and defect energies. With this, it will be possible to study how the oxidization of the UHTCs is affected by the different chemical bonding, defect density, and crystal orientation. The chemistry and microstructure of polycrystalline UHTC and UHTC composites will also be analyzed to see how the material's mechanical properties can be improved.

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List of Symbols, Abbreviations, and Acronyms

ARL	Army Research Laboratory
DEVCOM	US Army Combat Capabilities Development Command
DOD	Department of Defense
HPC	High-Performance Computing
LAMMPS	Large-scale Atomic/Molecular Massively Parallel Simulator
MD	molecular dynamics
NVT	Nosé–Hoover thermostat
ReaxFF	reactive force field
SiC	silicon carbide
SiO	silicon oxide
UHTC	ultra-high-temperature ceramic

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