Phase Field Modelling of TRISO SiC Layer Growth by Chemical Vapour Deposition

Phase Field Modelling of TRISO SiC Layer Growth by Chemical Vapour Deposition

by **GEORGES KARAGOZIAN**, B.Sc.

A thesis submitted to the School of Graduate Studies in partial fulfilment of the requirements for the Degree Master of Applied Science in Engineering Physics

McMaster University © Georges Karagozian, May 2025

McMaster University Masters of Applied Science (2025) Hamilton, Ontario (Engineering Physics)

TITLE: Phase Field Modelling of TRISO SiC Layer Growth by Chemical Vapour Deposition AUTHOR: Georges Karagozian, B.Sc. SUPERVISORS: M.J. Welland, M.H.A. Piro NUMBER OF PAGES: xvii, 113

LAY ABSTRACT

TRISO is a form of nuclear fuel that will be used in some advanced nuclear reactors. The TRISO fuel manufacturing process includes growing a layered structure using a technique called Fluidized Bed Chemical Vapour Deposition. Temperature, pressure, and concentration of gases used during the deposition process affect the structure and performance of the layers and consequently the entire fuel particle. The structure of the Silicon Carbide (SiC) layer is especially important because of its role in the overall structural integrity of the particle and is the heart of the safety case made by vendors to the regulators. To support the capability of predicting the microstructure of the SiC layer and to inform and optimize experiments, this thesis developed a computational model of SiC deposition by CVD using a thermodynamically-informed phase field model. The results demonstrate qualitative agreement with experimental images and quantitative agreement with experimental results of deposition rates.

ABSTRACT

The layers of TRISO (TRistructural ISOtropic) particles are manufactured by Fluidized Bed Chemical Vapour Deposition (FB-CVD). The microstructures of the Inner Pyrolitic Carbon (IPyC), Outer Pyrolitic Carbon (OPyC), and SiC layers are affected by the manufacturing conditions of temperature, pressure, and precursor gas concentration during the CVD process. The microstructure and grain morphology of the SiC layer is important since it affects the strength of the adhesion between IPyC-SiC and OPyC-SiC layers as well as the overall integrity of the fuel particle, and permeability of certain elements. Understanding the relationship between the fluidized bed parameters and microstructure facilitates scaling and optimizing particle production and particle performance.

Phase field modelling is a proven robust tool for predicting mesoscale phenomena such as microstructure evolution. A thermodynamically informed phase field model was developed to simulate the deposition of the SiC layer during the CVD process. This work presents results of modelling the nucleation, growth, microstructure evolution, and the columnar to equiaxed grain transition; as well as advances in multiphase, polygranular, and stoichiometric phase implementation, density variation between phases, and the use of the computationally efficient Geometric Multigrid (GM) solver in the Firedrake finite element code. The implementation of the GM solver resulted in a significant gain in computational efficiency and enabled the simulation of experimentally-relevant length-scales in 3 dimensions. The results were compared to layer growth data with good quantitative agreement and Electron Backscatter Diffraction (EBSD) images of the SiC layer in surrogate TRISO fuel with good qualitative agreement.

Keywords: Phase field, TRISO, Chemical vapour deposition (CVD), Nuclear fuel, CALPHAD

ACKNOWLEDGEMENTS

I express my extreme gratitude and appreciation to my supervisors, Dr. Michael Welland and Dr. Markus Piro, for their valuable mentorship, constant guidance, patience, and unwavering support throughout my graduate studies. I thank them for enabling me to pursue a research topic that interests me and for multiple professional development opportunities. My success in graduate school and the rest of my career is greatly owed to them.

This thesis project commenced at Ontario Tech University as a Master of Science in Modelling and Computational Sciences, continued as a student Co-Op work term at the Canadian Nuclear Laboratories in the Computational Techniques branch, and finished at McMaster University as a Master of Applied Science in Engineering Physics. I appreciate the funding, resources, and opportunities provided by these three institutions. Part of this research was also funded by the Discovery Grant and the Canada Research Chairs program (950-231328) of the Natural Sciences and Engineering Research Council of Canada.

I thank all my colleagues from the three institutions mentioned above, and particularly my colleagues in the Nuclear Fuels and Materials Group, for their guidance, support, productive discussions, and constructive feedback along the way.

Finally, I thank my family for their continued support while I pursue and achieve my goals, despite many hardships and setbacks.

CONTENTS

Lay Abstrac	i i	ii
Abstract	i	v
Acknowledg	ements	v
List of Figur	es i	х
List of Table	s xi	ii
Abbreviatio	ns xi	v
DeclareAch	eve xv	ii
1 Introduc	tion	1
2 Backgrou	ınd	4
2.1 TRIS	O Fuel	4
2.1.1	TRISO Design	5
2.1.2	Manufacturing Process.	5
2.1.3	Safety of TRISO Fuel	8
2.1.4	SiC Microstructure	8
2.2 Film	Deposition	9
2.2.1	Thin Films and Thin Film Deposition.	9
2.2.2	Chemical Vapour Deposition Process.	9
2.2.3	Nucleation and Growth Modes	0

	2.3	Modelling Tools.	11
		2.3.1 The CALPHAD Method	11
		2.3.2 Phase Field Modelling	13
3	Lite	erature Review	14
	3.1	TRISO Fuel History.	14
	3.2	SiC Deposition	16
	3.3	Relevant Phase Field Models	16
	3.4	Nucleation	19
		3.4.1 Methods of Implementing Nucleation into Phase Field	21
		3.4.1.1 Random Noise	21
		3.4.1.2 Deterministic/Discrete Nucleation	21
4	Met	thodology	22
	4.1	Phase Field Formulation	22
		4.1.1 Governing Equations.	23
	4.2	Current Approach	24
	4.3	Chemical Potentials	27
	4.4	Model Development	30
	4.5	Orientation dependence as a multiphase system	31
	4.6	Nucleation	31
		4.6.1 Nucleation by Decomposition.	32
		4.6.2 Spontaneous Nucleation.	33
	4.7	Simulation Geometry	33
	4.8	Solution Method	33
	4.9	Mesh Geometry	34

5	Res	sults & Discussion	36
	5.1	Model Testing.	37
		5.1.1 Columnar Growth	37
		5.1.2 Varying Radii	37
		5.1.3 Orientation dependent Interfacial Energy	41
		5.1.4 Nucleation by Decomposition	43
		5.1.4.1 With Initial Nuclei	43
		5.1.4.2 Without Initial Nuclei	43
		5.1.5 Discrete Random Nucleation	47
		5.1.5.1 Nucleation at $t = 0$ s	47
		5.1.5.2 Nucleation at $t > 0$ s	48
		5.1.6 Qualitative Comparison with Experiment	48
		5.1.7 Larger Scale Simulations	49
	5.2	SiC CVD Results	51
		5.2.1 Precursor Gas Ratio dependent Deposition Rate	51
		5.2.2 Polygranular SiC Growth by CVD	55
	5.3	Performance Comparisons	58
6	Con	nclusion	61
7	Rec	commendation For Future Work	64
Re	efere	nces	66
A	Fac	etSage Equilib Results	76
B	Pyt	hon Code	85
	B.1	Phase Field CVD Code	85
	B.2	Thermodynamic Potentials File	96
	B.3	Tools File	98
	B.4	Random Nuclei Generator	112

LIST OF FIGURES

2.1	TRISO fuel kernel micrograph (right) and examples of the two types of fuel compacts:	
	spherical (top) and prismatic (bottom)	6
2.2	TRISO fuel particles with 500 μm diameter UO_2 kernel on the left and 425 μm diameter	
	UCO kernel on the right	6
2.3	A diagram of FB-CVD reactor used for TRISO coating. Reproduced from Liu et al	7
2.4	A schematic illustrating the CVD process. Reproduced from Sun et al.	10
2.5	Thin film growth models	11
3.1	SiC deposition rate at varied temperatures as reproduced from Li et al.	17
3.2	SiC deposition rate at varied temperatures as reproduced from Yang et al.	17
3.3	SiC deposition rate dependence on partial pressure of MTS and H_2 at 1000°C as repro-	
	duced from Lu et al	18
3.4	Nucleation barrier ΔG dependence on the radius of the nucleus as adapted from Karthika	
	et al	20
4.1	Helmholtz energy a , mole fraction x , and phase variable ϕ behaviour at the interface	25
4.2	Demonstrative Gibbs energy potentials illustrating the equilibrium (lowest common tan-	
	gent solid black line), Taylor expansions (dashed line) of pure phases (solid coloured line)	
	and quadratic expansion (dotted line).	26
4.3	Quadratic energy surface plotted with the original phase potentials and lowest common	
	tangent	27
4.4	Phase diagram of MTS + H ₂	29
4.5	Gibbs energy curves for the gas solution and stoichiometric solid phases, along with the	
	lowest common tangent.	32

4.6	Schematic diagram of the CVD simulation.	34
4.7	Mesh geometry.	35
5.1	Simulation results showing isometric view (left column) and the morphology on the sub-	
	strate (right column). The stages of growth are a & e) time = 0 s showing initial nucleation	
	as separated 'islands' on the substrate; b & f) time = 0.006 s where islands have grown	
	uniformly until they contact each other; and c & g) 0.011 s and d & h) t=0.0140 s where	
	grains grow as columns vertically.	38
5.2	Variation of phase and species concentration starting at the substrate and moving through	
	an island, through the phase transition into the gas phase. Notable features are the con-	
	centrations following the diffuse phase interface and the absence of Argon in the solid	
	phase. "Phase" refers to the phase variable value of the solid phase. The variables are	
	non-dimensionalized, so the distance is in non-dimensional units.	39
5.3	Simulation results showing isometric view (left column) and the morphology on the sub-	
	strate (right column) with varying initial radii. The stages of growth are a & e) time = 0	
	s showing initial nucleation as separated 'islands' on the substrate; b & f) time = 0.005 s	
	where islands have grown uniformly until they contact each other; and c $\&$ g) time = 0.012	
	s and d & h) time = 0.04 s show columnar grow, coalescence of nuclei of the same grain,	
	and dissolution of smaller grains into the larger grains.	40
5.4	Simulation results showing isometric view (left column) and the morphology on the sub-	
	strate (right column) with orientation dependent interfacial energy. The stages of growth	
	are a & e) time = 0 s showing initial nucleation as separated 'islands' on the substrate; b &	
	f) time = 0.003 s where islands have grown uniformly until they contact each other; c & g)	
	time = 0.009 s and d & h) time = 0.015 s show columnar growth and coalescence of nuclei	
	of the same grain.	42

5.5	5 Simulation results showing isometric view (left column) and the morphology on the sub-	
	strate (right column) with 35 initial nuclei and nucleation modelled as decomposition.	
	The stages of growth are a & e) time = 0 s showing initial nucleation as separated 'islands'	
	on the substrate; b & f) time = 0.002 s where islands have grown uniformly until they con-	
	tact each other; c & g) time = 0.007 s and d & h) time = 0.01 s show columnar growth and	
	coalescence of nuclei of the same grain as well as the nucleation of equiaxed solid grain	
	ahead of the growing interface.	45
5.6	Simulation results showing isometric view (left column) and the morphology on the sub-	
	strate (right column) with orientation dependent interfacial energy. The stages of growth	
	are a & e) time = 0 s showing an empty domain b & f) time = 0.004 s and c & g) time =	
	0.019 s where there is a concentration change and slight phase variation, and d & h) time	
	= 0.031 s showing the nucleation of an equiaxed solid grain on the substrate	46
5.7	3D isometric view.	47
5.8	2D slice through the centre of the domain.	47
5.9	Random nucleation as initial conditions.	47
5.10) 3D aerial view	48
5.11	2D slice through the centre of the domain.	48
5.12	Random nucleation at random time steps.	48
5.13	EBSD image of the TRISO SiC layer between IPyC below and OPyC above obtained by	
	the Canadian Nuclear Laboratories. A cross-section of a phase field simulation result is	
	juxtaposed for qualitative comparison.	49
5.14	Simulation results showing isometric view (left column) and the morphology on the sub-	
	strate (right column) with 100 inital nuclei. The stages of growth are a & e) time = 0 s	
	showing an empty domain followed by b & f) time = 0.010 s and c & g) time = 0.042 s , and	
	d & h) time = 0.075 s showing growth. \ldots	50
5.15	SiC layer growth rate at varied ratios between the precursor gases for different tempera-	
	ture. The points represent the data obtained from the simulations and the dashed lines	
	are linear fits of the data	52

5.16 Simulation used to obtain growth rate data. (a & e) $t = 0$ s, (b & f) $t = 144.497$ s, (c & g)	
t = 640.257 s, and (d & h) t = 2026.63 s	54
5.17 A plot of parameters values over a line extending from the bottom to the top of the simu-	
lation domain. The snapshots correspond to the simulation of the growth rate stages: (a)	
Initial condition snapshot at t = 0 s, (b) t = 19.0481 s, (c) t = 57.0481 s, and (d) t = 85.3058 s.	55
5.18 Volume fraction of the solid phase over the length of the simulation at T = 1000°C, MTS: H_2	
= 1:1. ϕ_{total} is the phase field variable of the solid phases.	56
5.19 Polygranular SiC deposition by CVD. Aerial view from two different angles at 4 time steps.	
(a) Initial conditions with hundreds of nuclei on the bottom surface (b) random nucle-	
ation ahead of the interface (c) and (d) growth, with the final time step at t = 3000 s. \dots	57
5.20 Walltime as a function of degrees of freedom comparison between direct and GM solver.	
The top figure shows the results from both solver while the lower figure shows only the	
direct solver data for a clearer, magnified view	58
5.21 Memory usage as a function of degrees of freedom comparison between direct and GM	
solver. The top figure shows the results from both solver while the lower figure shows	
only the direct solver data for a clearer, magnified view.	59

LIST OF TABLES

2.1	Precursor gas and temperature used in the FB-CVD reactor to deposit TRISO layers. All	
	steps dilute the precursor gas in argon	8
2.2	Nucleation and Growth Regimes	12
2.3	Thin Film Growth Modes	12
4.1	Mole fraction of the Si-bearing gaseous species (x_{SiC}^{gas}).	28
4.2	Idealized Simulation Parameters	30
4.3	Material Properties of SiC and Ar	31
5.1	Scaling trends of walltime and peak memory usage for the direct and GM solvers, where	
	y represents the parameter in the column title, and n is the number of DoFs	60

ABBREVIATIONS

ACRONYMS	
AGR	Advanced Gas Reactor
BISO	Bi-Structural Isotropic
Ar	Argon
CALPHAD	Calculation of Phase Diagrams
CNSC	Canadian Nuclear Safety Commission
со	Carbon Monoxide
CVD	Chemical Vapour Deposition
сvі	Chemical Vapour Infiltration
DOF	Degrees of Freedom
EBSD	Electron Back Scatter Diffraction
FB-CVD	Fluidized Bed Chemical Vapour Deposition
FP	Fission Product
GB	Grain Boundary
GEM	Gibbs Energy Minimization
GenIV	Generation 4
HALEU	High Assay Low Enriched Uranium

HEU Highly Enriched Uranium
HTGR High Temperature Gas-cooled Reactor
HTR High Temperature Reactor
HTTR High Temperature Test Reactor
IPyC Inner Pyrolytic Carbon
LEU Low Enriched Uranium
MHTGR Modular High Temperature Gas-cooled Reactor
MTS
OPyC Outer Pyrolytic Carbon
PVD Physical Vapour Deposition
PyC Pyrolytic Carbon
SiC Silicon Carbide
SMR Small Modular Reactor
TAF-ID Thermodynamics of Advanced Fuels - International Database
THTR Thorium High Temperature Reactor
TRISO Tri-Structural Isotropic
UC Uranium Carbide
UCO Uranium Oxycarbide

Symbols

<i>a</i> Helmholtz energy density
c Concentration
C Celsius
g Gibbs energy density
J Flux
<i>R</i> Molar gas constant
<i>t</i> Time
T Temperature
V Volume
μ Chemical potential
ϕ Phase variable

DECLARATION OF ACADEMIC ACHIEVEMENT

The author hereby declares that all research, analysis, figures, results, computer code, and other items contained within this thesis are the work of the author, other than those referenced, as the sole contributor to this thesis.

1

INTRODUCTION

TRISO (TRistructural ISOtropic) particles are a form of advanced nuclear fuel intended to be used in multiple GenIV reactor concepts such as the designs being considered by vendors like X-Energy, Kairos Power, BWXT, and Westinghouse [1, 2]. TRISO fuel is of interest in the industry due to its robustness at high temperatures, which improves Fission Product (FP) retention and accident tolerance. These characteristics result from the layered structure of the TRISO particle, which is comprised of a fuel kernel coated with layers of buffer carbon, Inner Pyrolytic Carbon (IPyC), ceramic Silicon Carbide (SiC), and Outer Pyrolytic Carbon (OPyC). This design results in the nuclear fuel acting as a functional containment mechanism with layers of containment at the fuel level (namely, the nuclear fuel kernel, the fuel coating, and the fuel compact/matrix). The SiC layer acts as the primary containment vessel for FPs and provides structural integrity to the particle [1, 3, 4]. The manufacturing process of TRISO particles involves Chemical Vapour Deposition (CVD) to coat the kernel with sequential layers of buffer, IPyC, SiC, and OPyC. CVD is a scalable manufacturing technique that is well suited for the mass production of TRISO particles in a fluidized bed reactor. The microstructure of the PyC and SiC layers is affected by fluidized bed parameters, such as temperature, pressure, and precursor gas concentration during the CVD process [1, 5–7]. The microstructure and grain morphology of TRISO layers is important since it

affects the strength of the adhesion between the TRISO layers as well as the overall integrity of the fuel particle. Understanding the relationship between the fluidized bed parameters and microstructure facilitates scaling and optimizing particle production and particle performance.

Highlighting the importance of microstructure on the safety assurance, during the 2024 TRISO Focus Group meeting in Chalk River, Canada, a representative from the Canadian Nuclear Safety Commission (CNSC), said: "Up until very recently, all of the scientific literature concerning TRISO came exclusively from the US National Laboratories and it is difficult to challenge them. They are not reactor vendors, and they don't share the same perspective as the National Regulators" [8]. There are knowledge gaps regarding the microstructure of TRISO layers, the experimental parameters to produce different microstructures, and what microstructure is considered "good" or "safe"– especially from a regulator's perspective. It is therefore critical to understand and predict the microstructure of the TRISO layers produced during the CVD process as well as their effects on fuel performance and safety in-reactor.

Phase field modelling is a proven robust tool used across disciplines, capable of predicting phenomena of interest such as: thermodynamically driven microstructure evolution [9–11], thin-film deposition [12–18], subsurface grain evolution, such as columnar or equiaxed grain morphology and the transition between them [14, 15], and the ability to accommodate extreme conditions found in nuclear systems [19]. CALPHAD (CALculation of PHAse Diagrams) is a method of developing thermodynamic models for materials and computationally predict the phases that are stable at equilibrium starting from the Gibbs energies of the constituent species present in the system of interest, their corresponding concentrations, temperature, and pressure of the system [20, 21]. The CALPHAD method is a well-developed and reliable tool used by both academia and industry [22, 23].

To address the knowledge gap in the relationship between the deposition parameters and microstructure of the resulting SiC layer, a CALPHAD-informed phase field model was developed in this work to predict the microstructure of the SiC TRISO layer grown by CVD as a function of the fluidized bed parameters such as temperature, pressure, concentration, and species of the precursor gas. The primary objective of the model is to aid the optimization of these parameters and inform experiments supporting TRISO manufacturing capability in Canada. The model accounts for the thermodynamic potentials of the species present, the density variation between phases, and 3D multiphase grain nucleation and growth. Furthermore, this simulation framework takes advantage of the computationally efficient multigrid solver to simulate larger, experimentally relevant length and time scales on table-top computers.

This thesis will start by laying out the background knowledge about TRISO fuels and the role of the SiC layer in the safety and performance of the fuel, thin film deposition, and the modelling tools used (namely, CALPHAD and Phase field methods) in Chapter 2. A literature review of phase field models relevant to this work is summarized in Chapter 3. The methodology including the current approach and formulation of the phase field model, nucleation theory and implementation, model development efforts, simulation geometry, and solution methods is described in Chapter 4. Then, the results are presented and discussed in Chapter 5 followed by the conclusion in Chapter 6 and recommendations for future work in Chapter 7.

2

BACKGROUND

The background chapter aims to introduce the reader to the various topics that come together to perform the current work. First, TRISO fuel is introduced, discussing its purpose, design and specifications, manufacturing process, and safety features, as well as the microstructure of the SiC layer and the failure modes of the layer. Then, thin film deposition, nucleation, growth modes, and chemical vapour deposition are introduced. Finally, the modelling tools used in the current work are introduced, namely, the CALPHAD method and phase field modelling.

2.1. TRISO FUEL

Coated particle fuel development dates back to the 1950s, with variants of TRISO fuel being designed, developed, and tested in the USA, UK, and Germany starting in the 1960s for use in high temperature gas reactors under the Dragon program, as well as independently by Japan and China later [24]. Currently, TRISO is being considered as a fuel for GenIV reactor concepts due to the multilayer design, which makes the fuel robust and safe at higher operating temperatures and provides a functional containment mechanism for smaller reactor designs aiming to reduce construction costs and reactor footprint.

2.1.1. TRISO DESIGN

The fuel is shown in Figure 2.2 and consists of the following layers, respectively [24]:

- Fuel kernel: Spherical UCO fuel kernel with a diameter of 415 to $435 \mu m$ [25].
- Buffer layer: Porous carbon layer surrounding the fuel kernel at a thickness of 95 to $115 \mu m$. Provides space for gaseous FPs to diffuse in without adding pressure to the other layers [25].
- Inner pyrolytic carbon (IPyC): Thickness of 36 to 44 µm. Protects the kernel from chlorine compounds during SiC deposition, protects SiC from gaseous CO, shrinks under irradiation providing a compressive stress to counteract the internal pressurization stress on the SiC layer during operation [25].
- Ceramic silicon carbide (SiC): The main layer for containment, providing structural integrity and fission product retention. Thickness of 32 to 38 μm [25].
- Outer pyrolytic carbon (OPyC): Thickness of 36 to 44 μm. It's main purpose is to protect the SiC layer from mechanical stresses during the handling, overcoating, and compacting stages as well as provide an additional FP retention layer in the rare case of complete SiC failure [25].

The fuel particles are then overcoated by carbon and eventually compacted into either a spherical fuel compact for use in pebble bed reactors or cylindrical fuel pellets for prismatic core reactors as shown Figure 2.1 [24].

2.1.2. MANUFACTURING PROCESS

The production of the fuel kernels is done using the sol-gel process [26–28]. TRISO fuel typically uses HALEU (High Assay Low Enriched Uranium) UCO kernels with enrichment of 5-20%. The process starts with dissolution of uranium dioxide in nitric acid to make uranyl nitrate solution and carbon black is added to the solution as the source for carbon. An ammonia-donor chemical is added to the solution, the solution is cooled, then discrete droplets are dropped onto a hot organic solution (typically silicone oil in more recent work) forming uniform spherical gels containing uranium trioxide



Figure 2.1: TRISO fuel kernel micrograph (right) and examples of the two types of fuel compacts: spherical (top) and prismatic (bottom) [24].



Figure 2.2: TRISO fuel particles with 500 μm diameter UO_2 kernel on the left and 425 μm diameter UCO kernel on the right [24].



Figure 2.3: A diagram of FB-CVD reactor used for TRISO coating. Reproduced from Liu et al [5].

and carbon particles. The kernels are then calcined at 550 °C to convert the UO_3 to UO_2 , then sintered at 1550 °C with Ar-%1 CO then again with Ar-%3 CO atmosphere to produce the final UO_2 - UC_2 kernels [26, 28].

The fuel kernels are coated inside a fluidized bed (FB) reactor in which spherical fuel kernels are placed in a cylindrical chamber and gas is forced through a nozzle at the bottom of the chamber, pushing the solid particles up and making the ensemble of particles behave like a "fluid". In this well-mixed 'fluid', the kernels are coated via Fluidized Bed CVD (FB-CVD) through added chemicals. The nature of the coated layer is controlled by the species of gas flowing through the nozzle [1, 5, 25]. The precursor gas is diluted in an argon atmosphere and the nature of the precursor gas is changed at each stage of the coating process to produce the desired layer. The parameters used for TRISO coating are summarized in Table 2.1 and a schematic diagram of the process is shown in Figure 2.3.

Once the FB-CVD process is complete, the particles are overcoated with graphite to protect the particles from cracking while they're compacted into pebbles or pellets, and finally, the matrix is carbonized and heat treated.

Layer	Precursor gas	Temperature °C
Buffer	acetylene	1420
IPyC, OPyC	acetylene and propylene	1310, 1350
SiC	hydrogen and methyltrichlorosilane (MTS)	1565

Table 2.1: Precursor gas and temperature used in the FB-CVD reactor to deposit TRISO layers. All steps dilute the precursor gas in argon [1, 5, 25].

2.1.3. SAFETY OF TRISO FUEL

The highlighted safety features of TRISO fuel are its robustness and durability at high temperatures for using in high temperature reactors as well as the containment of FPs within the fuel, making it inherently safer in severe accident scenarios [1, 24, 25]. These features are achieved by the layered fuel design, and particularly the ceramic SiC layer discussed below.

2.1.4. SIC MICROSTRUCTURE

The SiC layer plays the role of the primary containment vessel for the TRISO particle, and its microstructure affects the diffusion rates of FPs through it [25]. The safety case of TRISO fuel relies on the microstructure of the SiC layer [1, 8]. The SiC microstructure as deposited on top of the IPyC layer can be the source of failure mechanisms of a TRISO particle such as [25, 29]:

- CO attack of the SiC layer: Fractured IPyC allows for CO gas to corrode the SiC resulting in FP release. It's reported that SiC microstructure engineering can be used to limit the CO corrosion by increasing the fraction of Σ 3 GBs [7].
- Non-retentive SiC layer: The SiC layer is permeable to FPs, if combined with PyC fracture could lead to TRISO failure. This is due to either long columnar grains, which allow for Grain Boundary (GB) diffusion of FPs in the radial direction, or small grains resulting in a high density of GBs, which also allows for faster GB diffusion of the FPs. The ideal temperature for depositing SiC using CVD is in the range of 1500-1700 °C. Higher temperatures closer to 1700 °C result in larger columnar grains, while lower temperatures (e.g., 1500 °C) result in moderately sized equiaxed grains. The moderate sized equiaxed grains are preferable for FP retention since the GBs result in a more tortuous path for the FP to diffuse through [25, 29].
- Debonding between IPyC and SiC: Debonding often leads to SiC fracture as observed in during

the AGR-1 campaign after which it was addressed by modifying the experimental parameters to weaken the buffer-IPyC bond. Porous IPyC combined with Chemical Vapour Infiltration (CVI) of the SiC into the pores before growing would result in a stronger SiC-IPyC bond. Both SiC-IPyC and buffer-IPyC interfaces can be investigated by CVI models [25, 29].

2.2. FILM DEPOSITION

2.2.1. THIN FILMS AND THIN FILM DEPOSITION

The term "thin film" refers to a relatively thin layer (nano-to-micrometer scale) of material deposited on a substrate. The small physical size implies potential interfacial energy contributions to the bulk behaviour of the material, meaning that the process is affected by mesoscale mechanisms.

CVD is defined as: The process used to coat a substrate (material to be coated) with a solid compound. In CVD, the precursor gas contains the material to be deposited, which undergoes a chemical reaction on the surface of the substrate to build the layer [30].

2.2.2. CHEMICAL VAPOUR DEPOSITION PROCESS

CVD is a well-established industrial process used to coat materials ranging from semiconductors to structural aerospace components. The process is visualized in Figure 2.4 and the steps are as follows [31, 32]:

- 1. Reactants, one of which contains the compound to be deposited as the coating, are transported near the substrate surface in the form of bulk gaseous flow.
- 2. The reactants diffuse to the substrate surface.
- 3. Adsorption of the reactants onto the substrate surface.
- 4. Chemical reaction between reactants on the surface.
- 5. Surface diffusion and lattice incorporation of the coating compound.
- 6. Desorption followed by diffusion of other reaction products away from the surface.
- 7. Reaction products transport by diffusion out of the deposition zone.



Figure 2.4: A schematic illustrating the CVD process. Reproduced from Sun et al. [33].

2.2.3. NUCLEATION AND GROWTH MODES

The CVD process is initiated by the adsorption of the deposit material onto the substrate surface as clusters of atoms, constituting the nucleation stage, followed by the growth stage. In the following context, "embryo" and "nucleus" refer to collections of atoms. Embryos can be categorized into three groups based on their size. Embryos below a certain size (critical radius) are described as subcritical and have a higher probability of dissolving because their growth is not energetically favourable. Embryos at the critical radius are in an unstable equilibrium between dissolution and growth. A supercritical embryo is energetically favourable to grow and become a nucleus, and the coalescence of such nuclei produces macroscopic deposits, which form continuous films. Nucleation determines the structure of the deposit formed and the mechanical and chemical properties of the CVD film formed [31, 32]. This relationship between nucleation regimes and growth modes depend on mesoscale thermodynamics, i.e. the balance between the bulk thermodynamic energy and the interfacial energy , and surface reactions with atoms adsorbed on the surface. The mechanisms and corresponding conditions, and descriptions are summarized in Table 2.2 and visualized in Figure 2.5.

A summary of the deposited microstructure resulting from temperature and precursor concentrations is presented in Table 2.3 [32]. The resulting structure is also influenced by the underlying substrate and the transport phenomena in the reactor. Parameters such as gas flow velocity, temperature and concentration gradients, convection on the surface of the substrate due to temperature difference, reactor geometry and the nature of the gas [34].





Frank-van der Merwe

Stranski-Krastanov







Volmer-Weber

Polycrystalline

Columnar

Figure 2.5: Thin film growth models [34].

2.3. MODELLING TOOLS

2.3.1. THE CALPHAD METHOD

The CALPHAD (CALculation of PHAse Diagram) method is a systemic approach of modelling the thermodynamic behaviour of material based on empirically obtained data [20]. In this approach, the system of interest is explored experimentally by preparing samples at varied compositions and finding thermodynamic properties such as heat capacity and phase boundaries as a function of temperature using techniques such as differential scanning calorimetry or laser flash analysis. After obtaining the experimental data and mapping the temperature-vs-composition phase diagram, the data is fitted using an appropriate thermodynamic model using commercially available software such as FactSage [36] or Thermo-Calc [37]. These models represent the thermodynamic energy of species and interaction parameters and are stored in thermodynamic databases such as ChemSage [38] or TAF-ID [39] databases to later be used to computationally reproduce phase diagrams using commercial software such as FactSage [36] or ThermoCalc [37] or open source software such as OpenCalphad [40] or Thermochimica [22].

At its core, the calculation of stable phases at a given temperature and composition is an optimization problem where, for constant pressure, the Gibbs energy of the system is minimized. The aforementioned software are examples of Gibbs energy minimization (GEM) solvers, and integrating

Nucleation Regime	Conditions	Description
Random Nucleation	Low temperature, high flux,	Random deposition of atoms.
	flux greater than surface diffu-	Not enough time for surface
	sion.	diffusion or grain reorientation.
		Forms an amorphous struc-
		ture.
2D Nucleation	Adsorption energy onto the	Thin film forms as a 2D flat
(Frank–van der	substrate is greater than the	layer and grows layer-by-layer.
Merwe growth)	adsorption energy on another	
	adatom/surface kink.	
Equilibrium Adsorp-	Low incoming flux or high tem-	Depending on the equilibrium
tion Nucleation	perature. Fast evaporation	conditions, the film grows to a
	from the top layer combined	certain thickness and maintain
	with a limited deposition rate	that thickness.
	will result in a limited thickness	
	of film to be deposited.	
3D Nucleation (Bub-	Binding force between atoms is	Complete condensation. Bub-
bles) at Low Temper-	greater than the binding force	bles form as isolated islands on
ature (Volmer–Weber	between atom and substrate.	the surface of bare substrate.
growth)	Re-evaporation rate is less than	
	formation rate.	
3D Nucleation (Bub-	Similar as above, but incom-	Incomplete condensation.
bles) at High Temper-	plete condensation. Some	Some atoms directly stick to
ature (Volmer–Weber	atoms evaporate.	already-formed bubbles.
growth)		
2D Then 3D (Stran-	Intermediate regime where de-	Flat layers form and grow, fol-
ski–Krastanov	position starts with 2D growth	lowed by bubbles above the flat
growth)	of the first layer, followed by 3D	layers.
	nucleation.	
Nucleation only at	Here the binding energy be-	Nucleation is only possible on
Defects	tween atoms and between	defective substrates, at the de-
	atoms and surface are low.	fects.

Table 2.2: Nucleation and Growth Regimes [31, 32, 35].

Table 2.3: Thin Film Growth Modes [34].

Condition	Crystal Structure
High Temperature	Monocrystalline
Medium Temperature	Polycrystalline
Low Temperature	Amorphous
Low Concentration	Monocrystalline
High Concentration	Amorphous

GEM into other codes to get a CALPHAD informed model can be a computationally expensive task.

In the context of this work, the Gibbs energy of the phases, as determined by CALPHAD, is used

to inform the potential energy of the bulk phases in the phase-field model, extending the equilibrium information to transient mesoscale phenomena.

2.3.2. Phase Field Modelling

Phase field modelling is a versatile technique used to study micro-scale and nano-scale material behaviour including complex interface morphology. Given that the model uses an energetic approach, it is relatively simple to include thermodynamic driving forces in the form of elastic, interfacial, bulk, electric, and magnetic energies, as well as transport phenomenon such as mass and heat transport (diffusion, convection, and conduction) [9, 10]. Phase field modelling has been used to study the growth of thin films using PVD [12, 16, 17], and CVD [18, 41]. The unique combinations of conditions and parameters such as surface adhesion and diffusion, subsurface dynamics, and vapor transport govern both the surface and subsurface morphology and features. It has been demonstrated that phase-field modelling of PVD can predict columnar grain structure with varying grain orientation angles in singlephase polycrystalline material [12, 17], columnar to equiaxed transition in polycrystalline grains [42], as well as the concentration modulation found in two-phase immiscible systems [14].

3

LITERATURE REVIEW

This chapter starts by going over the early history and development of TRISO fuel, the efforts of different countries during the last six decades, and the current status of adoption into GenIV reactors. The following section reviews the phase field literature relevant to the current work, highlighting efforts that are similar to the current effort and shortcomings of other models to motivate the relevance of the current work. Finally, nucleation is discussed, including methods of implementing it into phase field models.

3.1. TRISO FUEL HISTORY

The origin of coated particle fuel dates back to the Dragon project [43], a High Temperature Gas Reactor (HTGR) design by the United Kingdom, in the 1950s [24]. Starting out as a single layer of pyrocarbon coating, followed by a bilayer pyrocarbon coating (BISO), and eventually introducing the ceramic SiC layer for a significant increase in strength and FP retention. TRISO demonstration projects started in the 1960s with the Dragon reactor, a prismatic core HTGR, going critical in 1964 in the UK. Followed by the Arbeitsgemeinschaft Versuchsreaktor (AVR), the first pebble-bed reactor, in Germany starting operation in 1967 and continuing into the late 1980s. And the Peach Bottom unit I, also a prismatic core HTGR, in the United States going critical in 1966 and shutdown in 1974 [24]. In addition to those demonstration reactors, prototype reactors were built in the US and Germany in the 1970s and 1980s. The Fort Saint Vrain (FSV) prismatic core reactor in the US utilized Highly Enriched Uranium (HEU) TRISO fuel and operated from 1976 to 1989 [24]. The Thorium High Temperature Reactor (THTR), a pebble bed reactor in Germany, went critical in 1983 and utilized Thorium and Uranium oxide BISO fuel until its shutdown in 1988 [24]. The US fabricated and tested fuel for the Modular High Temperature Gas Cooled Reactor (MHTGR) and New Production Reactor (NPR) in the early 1990s [24]. Although early fuel designs included LEU and HEU carbide and oxide fuel kernels, as well as different layered designs and materials, modern day TRISO fuel consists of LEU, adopted from the 1980s onward, in a UCO kernel with the 4-layer PyC and SiC coating [24].

Later on, Germany performed more tests on UO₂ kernel TRISO fuel from 2004 to 2010 in the HFR-Petten reactor in the Netherlands [24]. The US DOE started the AGR program in 2002 focusing on LEU UCO TRISO fuel qualification, producing data to support licensing of an HTGR, and is still underway [24, 44]. South Africa also joined the US in this effort along with Westinghouse to develop the Pebble Bed Modular Reactor (PBMR) in South Africa, and General Atomics and AREVA worked on developing the prismatic core reactor [24, 44].

China started with basic research on HTGR fuels in the 1970s and 1980s, followed by the development of the HTR-10, a pebble bed reactor, from 1983 to 2003 with criticality being achieved in 2000 [24]. Construction of the HTR-PM, a high temperature helium cooled modular reactor with a pebble bed design, started in 2012, achieved first criticality and then connected to the grid in 2021, and entered commercial operation in December 2023 becoming the first commercial GenIV, and first commercial TRISO-fueled, reactor [24, 45]. Japan started basic fuel research in the 1960s, followed by the development of the High Temperature Test Reactor (HTTR), which started construction in 1991 and achieved full power in 2000 [24]. The HTTR was a prismatic core reactor that used annular fuel compact [24]. Japan plans to use the HTTR for a hydrogen production demonstration process aimed to be completed by 2030, and HTGR demonstration designing is underway with the aim of achieving carbon neutrality in the transportation, steel making, and hydrogen production industries by 2050 [46].

Current TRISO fuel manufacturers in North America are X-Energy, producing spherical TRISO

compacts [47], Kairos Power, currently at the early stages of developing the processes to produce TRISO pebbles [48, 49], and BWXT, having extensive operational experience with manufacturing TRISO under the AGR program [50].

Kairos Power obtained approval on the licence to construct their Hermes reactor, a Flouride salt cooled pebble bed design demonstration reactor, from the US NRC, and has already started the construction with the aim of having it operational by 2027 [51]. And Hermes 2, another demonstration reactor by Kairos Power that will produce electricity, has also obtained construction approval [51]. In Canada, Westinghouse's e-Vinci prismatic core micro-reactor is currently undergoing the licensing process in Saskatchewan [52], and Alberta is exploring the option of deploying X-Energy's Xe-100 pebble bed SMR [53], which has successfully completed pre-licensing vendor design review with the CNSC [54]. On the fuel production front, Canadian Nuclear Laboratories successfully manufactured TRISO fuel annular compact as a part of their previous venture with the USNC, meaning that there is expertise and operational experience on this front as well [55].

3.2. SIC DEPOSITION

There are experimental studies in the literature studying the effects of the deposition parameters on the outcomes of depositing SiC by CVD. Some of these studies can provide empirical results to compare the phase field model against.

Figures 3.1 and 3.2 show the results published by Li et al and Yang et al respectively. These result show that the depositon rate of the SiC layer by CVD increases in direct proportion to the temperature of the system. Figure 3.3 by Lu et al shows that the deposition rate is directly proportional to the product of the partial pressure of MTS with the square root of the partial pressure of H₂. These examples of experimental work can be replicated computationally to help validate or tune the model.

3.3. Relevant Phase Field Models

Several applications of phase field modelling to thin film growth have already established the relevance of the technique to understand deposit morphology [18, 41], composition distribution [15], growth structure [59, 60], and columnar-to-equiaxed grain growth transition [42]. There are, however, a num-



Figure 3.1: SiC deposition rate at varied temperatures as reproduced from Li et al [56].



Figure 3.2: SiC deposition rate at varied temperatures as reproduced from Yang et al. [57].



Figure 3.3: SiC deposition rate dependence on partial pressure of MTS and H₂ at 1000°C as reproduced from Lu et al [58].

ber of shortfalls with these models that have been addressed in recent advances:

- 1. Many models are restricted to 2D surfaces or symmetries to reduce computational expense.
- 2. Previous models ignored density variation between phases due to a lack of theoretical understanding. This has been resolved in recent work [61, 62].
- 3. Integration with bulk thermodynamics (i.e.: the choice of Gibbs or Helmholtz potentials, depending on the model) is troublesome due to spurious contributions to interfacial energy, the dominant energy in determining microstructure and morphology. Models based on linearization permit control and elimination of this issue [63, 64].
- 4. Surface quantities, such as surface strain, adsorption, etc., have not been explicitly controllable within previous phase-field models, instead being implicitly determined. These quantities have been demonstrated to be controllable, elucidating the behaviour of nano-scale systems [65, 66].
- 5. Stoichiometric phases are difficult to account for within the standard Grand Potential formulation, which is based on equivalence of chemical potentials. Specifically, stoichiometric phases that are represented as Dirac delta functions do not have a well defined slope and this is an obstacle for other codes to handle due to the lack of a unique lowest common tangent line as
discussed by Piro et al. [67].

Within polygranular materials, grains are differentiated by their crystal orientation. Furthermore, misorientation between grains contributes to the grain-grain interfacial energy. There is not currently a widely-accepted method within the phase field community to incorporate orientation dependence in phase-field models, although some research groups have developed approaches [68]. For example, modelling of the coating of TRISO particles with SiC by PVD using phase field has been developed [12, 14, 17] in which an orientation field is applied with a potential energy that incorporates materialdependent variables. This approach ignores any coincident site lattice factors as well as the periodicity of the orientation angle. A CALPHAD-informed phase field model of SiC growth by melt-infiltration has also been developed for isothermal conditions [69]. Columnar-to-equiaxed transition of grains was modelled using phase field to simulate additive manufacturing using laser powder bed diffusion, this model tracks the undercooling ahead of the solidifying interface to triger the nucleation of new grains and capture the transition into equiaxed grains [42]. This would correspond to tracking the undercooling of the gaseous phase ahead of the growing SiC interface in the CVD model. It is worth noting that the models found in the literature are in 2D, whereas microstructure is controlled by the interfacial energies that are dependent on grain surface area which in turn scales differently in 2D and 3D.

3.4. NUCLEATION

Thin film deposition and growth begins by nucleation, where atoms collect to form a critical nucleus that is stable and can grow. The theory of nucleation and growth modes of thin films is discussed in section 2.2. To accurately capture the growth of the layers during CVD, and especially the different growth modes resulting in various grain sizes and orientations, such as the columnar-to-equiaxed transition or controlling average grain size, the nucleation of solid phase critical nuclei must be implemented in the phase field model.

Classical nucleation theory assumes that the Gibbs free energy difference of nucleating a particle is the sum of the interfacial and bulk energies as illustrated in Figure 3.4, which shows an energy barrier for nucleation dependent on the nucleus radius [70].



Figure 3.4: Nucleation barrier ΔG dependence on the radius of the nucleus as adapted from Karthika et al. [71]. Scaling trend of 1) the interface energy scaling with the surface area as a quadratic function of the radius in blue; 2) The Bulk energy scaling with the volume of the phase as a cubic function of the radius in orange, noting that bulk energy is always negative; and 3) The energy change of nucleating a new phase as the sum of the interface and bulk energy in green. The red line indicates the critical radius, below which an embryo will be unstable and dissolve, and a larger radius would grow.

3.4.1. METHODS OF IMPLEMENTING NUCLEATION INTO PHASE FIELD

Modelling nucleation in phase field is an ongoing challenge in the community, and there is no widely accepted method of implementation [72–75]. Computationally, abrupt introduction of a nucleus disrupts the time integration algorithm, forcing the model to adapt to smaller time steps with the implementation of each nucleus throughout the simulation, resulting in a highly inefficient and expensive computation. Two methods of implementing nucleation are discussed below.

3.4.1.1. RANDOM NOISE

With this method, a Langevin (i.e.: Random) noise term is added to the phase variable to randomly nucleate a phase change. However, adding random noise at every time step disrupts the time integration algorithm of the model, and for this method to work, it generally needs an unphysically strong noise term to create a supercritical nucleus [72].

3.4.1.2. DETERMINISTIC/DISCRETE NUCLEATION

Explicit seeding introduces supercritical nuclei to the system at a given location and time. The time and location can be selected out of a statistical distribution, which can be used to populate an array of time and location for nuclei to appear before starting the simulation [72, 73]. Alternatively, supercritical nuclei can be introduced based on the critical nucleation theory, where at each time step a random location is selected, the probability of nucleation (P) is calculated using classical nucleation theory, a random number (R) is generated between 0 and 1, and if P is greater than R then a supercritical nucleus is introduced [70, 73]. A common problem that arises with this method is complications with mass conservation by the sudden introduction of a nucleus large enough to be stable.

4

Methodology

This chapter starts by describing how phase field and CALPHAD approaches are conceptualized to model phase transitions and capture the effects of interfaces between adjacent phases, followed by introducing the phase field equations. Section 4.2 details the approach used in this work. Then, section 4.4 describes how the phase field approach was applied to simulate SiC CVD, including details about the CALPHAD-informed gibbs energy potentials and the material properties used, followed by section 4.6 describing the nucleation methods used in this work and how they were implemented, and section 4.7 where the assumptions and geometry used to prepare the simulations are outlined. And finally, section 4.8 details the software, hardware, and numerical methods used to perform the computations.

4.1. PHASE FIELD FORMULATION

Phase field modelling is based on non-equilibrium thermodynamics, driven by the thermodynamics of the bulk phases and interfacial energy describing the interface. The treatment of interfaces as diffuse phases between the bulk phases allows for complex grain morphology to emerge. CALPHAD is an equilibrium thermodynamic methodology that addresses bulk phases. Interfaces are typically introduced as an energy contribution in excess of the bulk phases localized to an interfacial region. In this work, the phase field method is applied to model interfaces and phase transitions of a multiphase system with solid-gas and solid-solid interfaces, driven by thermodynamic influences informed by CALPHAD. This approach effectively brings equilibrium macroscale CALPHAD information down to the mesoscale to inform the thermodynamics of the bulk phase in the non-equilibrium phase field simulation.

4.1.1. GOVERNING EQUATIONS

Phase field models are represented by a set of coupled partial differential equations describing the evolution of the phase variable $\phi(\vec{x}, t)$ where \vec{x} and t represent position and time, respectively. The phase variable is a scalar field that indicates which phases are present at a given point in space and time with $\phi = 0$ denoting the gas phase, $\phi = 1$ denoting the solid phases and $0 < \phi < 1$ indicating the diffuse interface between the phases. In this diffuse interface approach, the phase variable is interpolated as a smooth function represented by Eq. 4.1 to ensure stability against perturbations in the ϕ field, and that p(0) = p'(0) = p'(1) = 0 and p(1) = 1 [10, 73].

$$p(\phi) = \phi^3 (6\phi^2 - 15\phi + 10) \tag{4.1}$$

This interpolation is not applied when it is desired to introduce decomposition, as described later in section 4.6 and shown in section 5.1.4. In the following notation, the subscripts will denote the species *i*, and the superscript will denote the phase π at a given spatiotemporal point. The vectorization of the variables is related to the multiphase formulation described in section 4.5. The coupled PDEs describing the evolution of the non-conserved field variables $\vec{\phi}(\vec{x}, t)$ and $\vec{c}(\vec{x}, t)$, where $\vec{c}(\vec{x}, t)$ is the conserved field variable for the concentration of species, take the form of Eqs. [4.2, 4.3] [9, 10]:

$$\frac{\partial \vec{\phi}}{\partial t} = -M_{\phi} \frac{\partial a}{\partial \vec{\phi}} \tag{4.2}$$

$$\frac{\partial \vec{c^{\pi}}}{\partial t} = \nabla \cdot \frac{\vec{D}}{RT} \nabla \frac{\partial a}{\partial \vec{c}}$$
(4.3)

where M_{ϕ} is the mobility term of the phase field, \vec{D} is the diffusion coefficient of the species with concentration \vec{c} , and a is the Helmholtz energy, which includes the terms for the bulk and interfacial energies. The interface emerges from the solution of the functional in Eq. 4.4 which defines the interface width and energy,

$$F_{\rm int} = \frac{3\sigma}{d} \frac{\partial (\phi^2 (1-\phi)^2)}{\partial \phi} + (6\sigma d)^2 \nabla^2 \phi$$
(4.4)

where σ and d are the interfacial energy and the interfacial width, respectively.

4.2. CURRENT APPROACH

Phase-field models have the potential to unite transport, equilibrium thermodynamics, phase transformation kinetics, and interfacial effects, but are hindered by computational expense and unintended interfacial properties. Therefore, a generalized approach was developed to incorporate thermodynamic potentials while controlling implicit interfacial energy contributions using the principle of local equilibrium. Figure 4.1 illustrates the Gibbs interface [76], where the dashed lines represent the sharp interface treatment (step function at the interface) and the solid lines represent the diffuse interface treatment (that is, the phase variable ϕ as a smooth function ranging from 0 to 1 at the interface). This effectively separates the Helmholtz energy as:

$$a = a^{\text{bulk}} + a^{\text{interface}} \tag{4.5}$$

Equations 4.2 and 4.3 show that transport equations can be expressed in terms of the Helmholtz energy potential of the system. This work makes the assumption that the volume of phase π is related directly to the phase field variable,

$$V^{\pi} = p(\phi^{\pi}) \tag{4.6}$$

which simplifies the following mathematical derivation.

The dynamic variables are the local concentrations of species *i*, c_i , and volumes of phase π , $V^{\pi}(\phi^{\pi})$. Since the phase transformation occurs under constant c_i and V^{π} the relevant thermodynamic poten-



Figure 4.1: Helmholtz energy a, mole fraction x, and phase variable ϕ behaviour at the interface [77].

tial is the Helmholtz energy $a(c_i, V^{\pi})$. However, most thermodynamic databases record the Gibbs energy (g), which is a function of temperature, concentration, and pressure. Therefore, the Helmholtz energy is obtained by $a = g + a^{el}$ with

$$a^{\pi} \left(c_{i}^{\pi}, V^{\pi} \right) = g^{\pi} \left(c_{i}^{\pi}, P^{\pi} \right) + \frac{1}{2} V_{0} \kappa \ln^{2} \left(\frac{V^{\pi}(\phi^{\pi})}{V_{0}} \right)$$
(4.7)

where κ is the bulk modulus of the given phase. The volume at zero pressure is given by $V_0 = \sum_i c_i v_i$ where v_i are the specific volumes of species *i*, and this elastic energy term captures the density variation between phases [61].

It is now assumed that for the coexistence of phases with Helmholtz energy $a^{\pi}(c_i^{\pi}, V^{\pi})$, internal processes are fast enough so as to minimize the local energy described by a composite potential $a(c_i, V^{\pi})$. The composite potential a is the approximation of the minimizing sum of all individual phase potentials $a^{\pi}(c_i^{\pi}, V^{\pi})$ subject to mass constraints [11, 64],

$$a(c_i, V^{\pi}) = \min_{c_i = \sum_{\pi} c_i^{\pi}} \sum_{\pi} a^{\pi}(c_i, V^{\pi})$$
(4.8)

This formulation naturally includes the Helmholtz energy and its common role in Eqs. 4.1 and 4.3 leads to a thermodynamically self-consistent model. If a^{π} is expanded as a quadratic about a known state, obtained for example through a GEM, Eq. (4.8) becomes a equality constrained quadratic programming problem.

An example of a thermodynamic system is shown in Figure 4.2 where phases α and β are approximated by a second order Taylor expansion, α_T and β_T . The result of minimizing the Helmholtz potential subject to the equality constraint is shown in Figure 4.3 with end members α_q and β_q in Figure 4.2.

Here, the phase indicator function $p(\phi)$ from Eq. 4.1 is interpreted to be the volume of phase β , and *c* to be the overall concentration, resulting in:

$$a^{bulk}(c,p) = \min\left[a^{\alpha}(c^{\alpha},p) + a^{\beta}(c^{\beta},1-p)\right]$$
 (4.9)

with

$$\vec{c} = \vec{c^{\alpha}} + \vec{c}^{\beta} \tag{4.10}$$

And a minimum surface $a_q^{\text{bulk}}(c, p)$ that is the quadratic approximation of eq. 4.9 in *c* and *p*. The quadratic composite is compared to the true minimization of eq 4.8 shown in Figure 4.3.



Figure 4.2: Demonstrative Gibbs energy potentials illustrating the equilibrium (lowest common tangent solid black line), Taylor expansions (dashed line) of pure phases (solid coloured line) and quadratic expansion (dotted line).



Figure 4.3: Quadratic energy surface plotted with the original phase potentials and lowest common tangent.

A significant benefit to this approach, and the use of p^{π} as the volume of phase π , is that *a* is a quadratic in all dynamic variables, and the linearization of thermodynamic driving forces in eqs 4.1 and 4.3. This simple form is numerically stable, which lends itself to geometric multigrid solvers which enable large systems to be examined [77]. A potential downside of the quadratic approximation could be the possibility of obtaining negative solutions, i.e. negative concentration values.

4.3. CHEMICAL POTENTIALS

The deposition of SiC by CVD usually occurs by a chemical reaction between hydrogen and a siliconhydrocarbon gas in the presence of argon or nitrogen at temperatures between 1250 – 1700°C [1, 6]. Here, it is considered that the reaction of Methyltrichlorosilane (MTS) with hydrogen in the presence of argon produces SiC and other byproducts depending on the conditions [1, 6, 78, 79]. The equilibrium phase diagram of MTS + H_2 was calculated using the Phase Diagram module in FactSage version 8.0, with the included FactPS database, at a pressure of 1 atm and a temperature range of 300 to 1800°C to obtain the phase diagram shown in Figure 4.4 [36]. The phase diagram was intended to provide a general idea of the phase space under the FB-CVD conditions. Ar gas was not included since it is an inert gas and spectator during the reaction.

A series of point calculations were performed using the FactSage Equilib module at 1 atm at different temperatures and molar ratios between MTS and H₂ gas with an Ar cover gas at 1:1 molar ratio to H₂, one example of the Equilib calculation results is shown in Appendix A. These results are used to find the mole fraction of the Si-bearing gaseous species present at equilibrium x_{SiC}^{gas} , tabulated in Table 4.1, to be used later to approximate a proxy SiC gas. The reference Gibbs energy functions were obtained directly from the FactPS database in FactSage version 8.0. The potential of β -SiC (Cubic crystal in the solid phase) is shown in Eq. 4.11, for Ar gas in Eq. 4.12.

Table 4.1: Mole fraction of the Si-bearing gaseous species (x_{SiC}^{gas}) .

Temperature (°C)	MTS:H ₂					
	1:1	1:2	1:4	1:36	1:50	1:70
1000	5.4499e-02	3.6355e-02	1.8888e-02	3.8206e-04	2.3289e-4	1.4289e-04
1200	4.1749e-02	2.4390e-02	9.7347e-03	1.6331e-04	1.1467e-04	8.0482e-05
1400	3.8288e-02	2.1013e-02	8.4300e-03	1.5132e-4	1.0784e-4	7.6452E-05

$$g_{SiC}^{\text{solid},0}(T) = \begin{cases} -37054.710 + 413.92168T - 59.088157T \text{Ln}(T) - 225504.83T^{-1} - \\ 11126.909 \text{Ln}(T) & 295 < T < 1400 \\ -73117.225 + 459.73319T - 63.088778T \text{Ln}(T) + 673617.13T^{-1} - \\ 2255.2160 \text{Ln}(T) - 1400.7714T^{0.5} & 1400 \le T < 4000 \end{cases}$$

$$(4.11)$$

 $g_{Ar}^{gas,0}(T) = -6197.3459 - 15.628755T - 20.786T \text{Ln}(T) \qquad 295 < T < 6000 \qquad (4.12)$



Figure 4.4: Phase diagram of MTS + H₂.

The reaction of MTS with H_2 to produce SiC typically occurs at the substrate surface, as described in the CVD process steps in section 2.2.2. If the reaction kinetics are fast enough, CVD steps 3-6 occur effectively instantaneously, and the process is limited by diffusion of the precursors in the gas phase. As a pragmatic simplification to avoid simulating multiple species (with poorly known diffusion coefficients, convective currents, and reaction kinetics), the reaction is considered to have occurred outside of the simulation domain and an effective SiC gaseous species diffusing in the gas phase and precipitating onto the surface. The chemical potential of this virtual species is the same as the product of the precursor reaction, and depletion in the gas phase is still captured. At steady state, there will be an amount of gaseous SiC at equilibrium with solid SiC, i.e. Eq. 4.13.

$$\mu_{\text{SiC}}^{\text{gas}} = g_{SiC}^{\text{gas},0} + RT \ln(\mathbf{x}_{\text{SiC}}^{\text{gas}}) = g_{\text{SiC}}^{\text{solid},0}$$
(4.13)

So, the reference Gibbs energy of the proxy SiC gas is estimated by Eq. 4.14, where R is the gas constant and x_{SiC}^{gas} is the molar fraction discussed earlier.

$$g_{\rm SiC}^{\rm gas,0}(T) = g_{\rm SiC}^{\rm solid,0}(T) - RT \ln(x_{\rm SiC}^{\rm gas})$$

$$\tag{4.14}$$

The reference molar Gibbs energies $g_{SiC}^{solid,0}$, $g_{SiC}^{gas,0}$, and $g_{Ar}^{gas,0}$ are obtained from Eqs. 4.11, 4.12, 4.14.

4.4. MODEL DEVELOPMENT

The reference Gibbs energy potentials were obtained as discussed above. The material properties of SiC and Ar are summarized in Table 4.3, with the argon density calculated using the ideal gas law. The Gibbs energy potentials are calculated using Eqs (4.15) and (4.16). The concentration of the SiC species in the solid and gas phases are c_{SiC}^{solid} and c_{SiC}^{gas} , respectively. The gas phase also contains argon with concentration, c_{Ar}^{gas} . The temperature, *T*, is an input that can be varied. The early stage of model development, with results shown in section 5.1, used idealized parameters summarized in Table 4.2. The SiC CVD model, with the results shown in section 5.2, used material properties obtained from the literature, and summarized in Table 4.3, with the argon density calculated using the ideal gas law.

Parameter	Value	
$ ho_{ m SiC}$	1	
$\kappa_{ m SiC}$	1×10^{6}	
$ ho_{ m Ar}$	1	
κ _{Ar}	1×10^4	
D _{solid}	1×10^{-3}	
D _{gas}	1×10^{-3}	
Solid-solid interface energy	1×10^{5}	
Solid-gas interface energy	1×10^{5}	
М	1×10^{-3}	
Interface width	0.2	

Table 4.2: Idealized Simulation Parameters

$$g^{gas}(c_{SiC}^{gas}, c_{Ar}^{gas}, T) = c_{SiC}^{gas} \left(g_{SiC}^{gas,0} + RT \ln\left(\frac{c_{SiC}^{gas}}{c_{SiC}^{gas} + c_{Ar}^{gas}}\right) \right) + c_{Ar}^{gas} \left(g_{Ar}^{gas,0} + RT \ln\left(\frac{c_{Ar}^{gas}}{c_{SiC}^{gas} + c_{Ar}^{gas}}\right) \right)$$
(4.15)

$$g^{solid}(c_{SiC}^{solid}, T) = c_{SiC}^{solid} g_{SiC}^{solid,0}$$
(4.16)

Parameter	Value		
$ ho_{ m SiC}$	3.09 g/cm ³		
$\kappa_{ m SiC}$	186 GPa		
$ ho_{ m Ar}$	$3.478 \times 10^{-4} \text{ g/cm}^3$		
$\kappa_{ m Ar}$	1.0132×10^{-4} GPa		
D _{solid}	$4 \times 10^{-18} \mathrm{m^2/s}$		
Dgas	$10^{-5} \mathrm{m^2/s}$		
SiC-SiC interface energy	$0.4 \text{J}/\text{m}^2$		
SiC-gas interface energy	2.24J/m^2		
М	$1 \times 10^{-7} \mathrm{m}^3/\mathrm{J}\cdot\mathrm{s}$		
Interface width	$5 \times 10^{-6} \mathrm{m}$		

Table 4.3: Material Properties of SiC and Ar [31, 69, 80-82].

The Gibbs energy potential curves for this system along with the lowest common tangent are shown in Figure 4.5. The stoichiometric solid phase appears as a vertical line [67]. The lowest common tangent, corresponding to bulk equilibrium, is depicted as a dashed line.

4.5. ORIENTATION DEPENDENCE AS A MULTIPHASE SYSTEM

Since the purpose of this work is to study the microstructural evolution and morphology of SiC, it is necessary to model grains at different grain orientations in the solid phase. However, there is no widely accepted method of modelling the effects of grain orientation on the interfacial energy in the literature [12, 83, 84]. In lieu of an orientation model, the current work implements the multiphase formulation with multiple SiC solid 'phases', each with a prescribed orientation [11]. This effectively discretizes the orientation, and interfacial energies can be based on it.

Following Eq. 4.8, the phase-specific concentrations are determined by partitioning the overall concentrations, c_{SiC} and c_{Ar} . The dynamic variables for the simulation are therefore, c_{SiC} , c_{Ar} , solved by associated instances of Eq. 4.3, and ϕ^{SiC_1} , ϕ^{SiC_2} , ϕ^{SiC_3} solved by Eq. 4.2.

4.6. NUCLEATION

The difficulty of capturing nucleation in a phase field model, and the lack of a widely accepted and an adequate method was discussed earlier in the literature review chapter. The random noise method is the most problematic and least promising out of the three methods discussed due to its effect on the



Figure 4.5: Gibbs energy curves for the gas solution and stoichiometric solid phases, along with the lowest common tangent.

time integration algorithm. The deterministic method is the next promising method to be tested to find the most suitable algorithm for implementation while avoiding mass conservation violation.

The challenges of nucleation in phase field modelling extend beyond selecting a suitable method to nucleate a phase and a treatment that avoids violating any conservation laws. Other factors to consider include the nucleus morphology at nucleation, the orientation of said nucleus if it has an asymmetric morphology, and the grain orientation. The factors are not considered in the current work, and need not be pursued if a sufficiently accurate model can be developed without them. Here, two methods for implementing nucleation in the model were explored in an effort to capture columnar-to-equiaxed grain growth transition.

4.6.1. NUCLEATION BY DECOMPOSITION

Decomposition was tested as a proxy for nucleation. This was achieved by avoiding the interpolation function in eq. 4.1 and setting $V^{\pi} = \phi^{\pi}$ instead, which causes the decomposition of metastable regions into either a solid or gas phase.

4.6.2. Spontaneous Nucleation

Homogeneous nucleation [73] was introduced into the simulation by discretely adding supercritical nuclei as the simulation progressed. To achieve this, three separate arrays were populated with: coordinates of nucleation site within the bounds of the simulated volume, phase or grain type (choice of 1 out of 3 solid SiC grains), and nucleation times. All arrays were sampled from a uniform distribution. These nuclei can be implemented at once at t = 0 as initial conditions or one-by-one at the sampled time steps for t > 0. Note that in the latter case it is possible to modify the nucleation rate based on the choice of the random distribution used to generate the pseudo-random numbers, although in this work only uniformly distributed time steps were used. Both cases of homogeneous nucleation at t = 0 and t > 0 were implemented in the current model.

4.7. SIMULATION GEOMETRY

The overall geometry of the simulations sets the substrate at the bottom with the incident SiC-carrying vapour permeating the entire volume at the start of the simulation, as depicted in the diagram in Figure 4.6. The transport of the incident vapour is governed by diffusion and held at a constant supply rate by setting a Dirichlet boundary condition at the top surface. To simplify the model and exclude the IPyC layer and related effects, the model assumes some deposited SiC on the substrate at the start of the simulation at the bottom of the domain. This is a good approximation because the main objective is understanding and modelling the grain structure within the SiC layer. Some of the simulations testing nucleation models exclude the initial SiC substrate and start with an empty domain (sections 5.1.4 and 5.1.5).

4.8. SOLUTION METHOD

The governing equations given by Eqs. (4.3, 4.2) are implemented and solved using the Firedrake finite element package [85] which used the linear back-end package Portable, Extensible Toolkit for Scientific Computation. An adaptive backward Euler implicit time integration algorithm is implemented for numerical robustness. A geometric multigrid (GM) method is used to solve the linear system with five levels of refinement, which scales well for multiple cores and deployable on high performance



Figure 4.6: Schematic diagram of the CVD simulation.

computing platforms [77]. The geometric multigrid method is a type of iterative differential equation solver that cycles between layers of coarse and fine grids to approximate the solution. All original code is included in Appendix B.

Simulations for the results shown in sections (5.1.1, 5.1.2, 5.1.3, 5.1.4) were run on 16 cores with peak RAM usage of 33 GB by the geometric multigrid solver. The rest of the simulations were run on a workstation with 24 cores and 256 GB of RAM. The results are visualized using Paraview [86] and represented as an aerial view as well as a 2D view from the bottom of the substrate to see the microstructure between the grain boundaries.

4.9. MESH GEOMETRY

The mesh was set to have tetrahedral elements. For the GM solver, the coarse mesh resolution was set to L/4, where L is the side length of the cubic domain normalized to 1. The fine mesh resolution was set to the interface width (d). The GM solver was set to use the V-cycle with 4 levels of refinement. Figure 4.7 shows the mesh. The finest detail that needed to be captured is the interface, which is why the fine mesh needs to be at the same scale of the interface width. A rough mesh sensitivity analysis was performed by running simulations with the fine mesh set to double, equal to, and half the inter-

face width. A fine mesh resolution equal to the interface width was deemed to be sufficient through numerical examination.



Figure 4.7: Mesh geometry.

4.10. DEPOSITION RATE CALCULATION

In order to obtain quantitative results to compare to experiments and evaluate the model, the growth rate of the solid phase was calculated. This was achieved by integrating the phase variable (ϕ) field over the volume of the simulation domain, and record the results for every time step. The results would indicate the fraction of the simulation volume occupied by a given phase. Taking the total fraction of solid phases, multiplying by the cross section of the growing solid phase front in meters results in a value of growth in meters, which then can be used to calculate the growth rate in units of m/s.

A simulation domain was set with a cube with sides of $100 \,\mu\text{m}$ and a flat single-grain solid phase substrate as initial condition. A series of simulations were run while varying the molar ratio between the precursor gases (MTS:H₂, ratios between 1:1 to 1:100), and the tests were repeated at three different temperatures (1000°C, 1200°C, 1400°C) to observe the influence of temperature and precursor gas concentration on the deposition rate. An average growth rate was calculated by taking the initial and final values of the phase fraction and time and performing the calculation mentioned above. The results were then converted to units of mg/cm²min to compare to the experimental results from the literature shown in Figure 3.3.

5

RESULTS & DISCUSSION

This thesis set out to develop a modelling capability to support efforts in TRISO manufacturing by providing a tool to predict and simulate the microstructure of the SiC layer. To do this, the phase field method was chosen as the modelling tool in addition to the CALPHAD-informed thermodynamic potentials to provide the information for the driving forces during the deposition process. As an original effort, this work has to be established from the foundation. Once the model was developed, idealized representative parameters were implemented, and then it was tested to determine that the desired phenomena were captured. This meant testing columnar growth (section 5.1.1), proper multiphase implementation as well as coarsening (section 5.1.2), the effects of orientation dependent interfacial energies (section 5.1.3), and the different methods and algorithms for nucleation to determine which one might be better suited for modelling the system of interest (sections 5.1.4 and 5.1.5). Then, the model was applied to the SiC CVD system with the implementation of material properties from the literature that was summarized in Table 4.3 (section 5.2). And finally, benchmark simulations were run to demonstrate the computational efficiency introduced by using the GM solver enabled by the quadratic approximation of the Gibbs energy potentials (section 5.3).

The results from each milestone of the simulations are presented in their respective subsections

below, starting with the earliest and simplest steps and moving forward from there. The translucent light blue box seen in some figures below represent the simulated volume permeated with the gaseous SiC + Ar phase. The nuclei surfaces represented where the phase variable value is at 0.5, with the centre of the nuclei being at a value of 1 representing the solid phase. The different colour maps of the nuclei represent the different grain orientations. It is worth clarifying that this work models a 2D flat substrate growth in 3D space as opposed to a 3D substrate (e.g.: deposition on a sphere). Yet a major improvement compared to models limited to 2D space.

5.1. MODEL TESTING

5.1.1. COLUMNAR GROWTH

Figure 5.1 shows a simulation of four phases (gas and three solid grains representing different grain orientations), starting with 12 nuclei at t=0 s on the bottom surface and growing. The spherical nuclei grow and contact other grains. If the grains are of different orientations (phases), this produces a grain-grain boundary between them, whereas if the grains are of the same orientation, the same grain nuclei merge into a larger grain. The grains then continue to grow in a columnar regime after the in-plane area is fully exhausted.

This test demonstrates the initial step during development and the successful modelling of homogeneous nucleation, the supply of precursor gas by the Dirichlet boundary condition on the top surface, and the columnar growth of solid SiC grains. Sample profiles of the phase field variable and the concentration of species, normalized to the total concentration in their phases, are shown through an island going in the z-direction in Figure 5.2. Herein, the diffuse interface as the phase value goes from 1 at the centre of the solid phase nucleus to 0 at the boundary, and the scale of the concentration variations, are shown.

5.1.2. VARYING RADII

The next test is to confirm coarsening between different grains during columnar growth. Figure 5.3 shows the results of a simulation starting with nuclei of different radii as the initial condition (i.e. homogeneous nucleation at t = 0 s). The results show the larger nuclei dominating, while the smaller



Figure 5.1: Simulation results showing isometric view (left column) and the morphology on the substrate (right column). The stages of growth are a & e) time = 0 s showing initial nucleation as separated 'islands' on the substrate; b & f) time = 0.006 s where islands have grown uniformly until they contact each other; and c & g) 0.011 s and d & h) t=0.0140 s where grains grow as columns vertically.



Figure 5.2: Variation of phase and species concentration starting at the substrate and moving through an island, through the phase transition into the gas phase. Notable features are the concentrations following the diffuse phase interface and the absence of Argon in the solid phase. "Phase" refers to the phase variable value of the solid phase. The variables are non-dimensionalized, so the distance is in non-dimensional units.

nuclei get enveloped by the larger grains and eventually coarsen and dissolve into the larger grains while columnar growth continues. This result confirms that the model captures the dissolution and coarsening of grains competing with columnar growth.







Figure 5.3: Simulation results showing isometric view (left column) and the morphology on the substrate (right column) with varying initial radii. The stages of growth are a & e) time = 0 s showing initial nucleation as separated 'islands' on the substrate; b & f) time = 0.005 s where islands have grown uniformly until they contact each other; and c & g) time = 0.012 s and d & h) time = 0.04 s show columnar grow, coalescence of nuclei of the same grain, and dissolution of smaller grains into the larger grains.

h

d

5.1.3. ORIENTATION DEPENDENT INTERFACIAL ENERGY

This test intended to explore the effects of grain misorientation dependent interfacial energy on the growth and morphology of the grains to identify whether it is an avenue worth pursuing in future work. The interfacial energy was deterministically varied between the different solid grains (a difference of one order of magnitude) to model grain orientation-dependent interfacial energy, i.e. the interfacial energy value between each solid-solid phase was hard-coded into the simulation to be different, and all the solid-gas interfacial energy were made to be equal, whereas the results shown in Figure 5.3 have equal interfacial energies between all phases. The results shown in Figure 5.4 indicate a slight difference in behaviour, namely, slower coarsening and dissolution of smaller grains when compared to the previous results as seen by the time step value of the subfigures.

Although the results are limited and qualitative in nature, they show that the current model is capable of capturing grain misorientation dependent interfacial energies and the results do encourage the pursuit of this approach in future work. However, since there aren't robust and accepted methods of implementing grain misorientation dependent interfacial energy between grains in the phase field literature, this avenue was not pursued any further in the current work.







Figure 5.4: Simulation results showing isometric view (left column) and the morphology on the substrate (right column) with orientation dependent interfacial energy. The stages of growth are a & e) time = 0 s showing initial nucleation as separated 'islands' on the substrate; b & f) time = 0.003 s where islands have grown uniformly until they contact each other; c & g) time = 0.009 s and d & h) time = 0.015 s show columnar growth and coalescence of nuclei of the same grain.

h

d

5.1.4. NUCLEATION BY DECOMPOSITION

As discussed in section 4.1.1, the interpolation function $p(\phi)$ is used as phase volume to ensure the stability of pure phases as $\frac{dp}{d\phi}(\phi = 0, 1) = 0$. If instead, it is allowed for $V^{\pi} = \phi^{\pi}$, phases may be driven to change phase spontaneously when $\frac{da}{d\phi} < 0$, as discussed in section 4.6. The mitigating force in this case is the penalty associated with forming an interface, which is already included in the phase field formulation. This choice raises the possibility of spontaneous phase change (akin to nucleation) ahead of the phase-front in a process similar to spinodal decomposition.

The method described in section 4.6.1 was used in two different configurations to assess whether this is a successful method to model equiaxed grain growth ahead of a columnar growing interface. First, decomposition was enabled in a simulation with existing nuclei on the substrate surface as an initial condition (homogeneous nucleation at t=0 s) with the results shown in Figure 5.5 and discussed in section 5.1.4.1. Additionally, decomposition was enabled in a simulation with no solid nuclei, permeated only by the gaseous phase with the results shown in Figure 5.6 and discussed in section 5.1.4.2.

5.1.4.1. WITH INITIAL NUCLEI

Figure 5.5 shows nucleation by decomposition ahead of the growing interface. Here, the SiC substrate grains set as initial conditions start with columnar growth, and then nucleation occurs ahead of the growing interface. In this case, the nucleating grains match the same orientation as the grains below them. This defeats the purpose of incorporating nucleation since the goal was to capture equiaxed grains blocking the growth of the columnar grains, but in this case the grains would simply join together to form a single large grain. Additionally, the model worked with non-physical amounts of gaseous SiC concentrations (i.e., the concentration of the gaseous species had to be artificially increased over the equilibrium amount to produce the results shown).

5.1.4.2. WITHOUT INITIAL NUCLEI

Figure 5.6 shows the simulation of an empty domain without initial nuclei while implementing nucleation by decomposition. An equiaxed solid grain is formed on the substrate; however, this model shares the same challenges mentioned in section 5.1.4.1 above. The results show the simulation domain (blue box) to visualize the change in the phase variable value before the appearance of a solid

phase as shown in Figure 5.6d.







Figure 5.5: Simulation results showing isometric view (left column) and the morphology on the substrate (right column) with 35 initial nuclei and nucleation modelled as decomposition. The stages of growth are a & e) time = 0 s showing initial nucleation as separated 'islands' on the substrate; b & f) time = 0.002 s where islands have grown uniformly until they contact each other; c & g) time = 0.007 s and d & h) time = 0.01 s show columnar growth and coalescence of nuclei of the same grain as well as the nucleation of equiaxed solid grain ahead of the growing interface.



Figure 5.6: Simulation results showing isometric view (left column) and the morphology on the substrate (right column) with orientation dependent interfacial energy. The stages of growth are a & e) time = 0 s showing an empty domain b & f) time = 0.004 s and c & g) time = 0.019 s where there is a concentration change and slight phase variation, and d & h) time = 0.031 s showing the nucleation of an equiaxed solid grain on the substrate.

5.1.5. DISCRETE RANDOM NUCLEATION

In this section, the results from testing random homogeneous nucleation are presented and discussed. The results are divided into two submethods:

- Nucleation at t = 0 s: The locations of the nuclei were randomly sampled from a uniform distribution within the bounds of the simulated domain and all the nuclei were inserted as initial conditions.
- Nucleation at t > 0 s: Here, that nucleation time steps were also sampled from a uniform random distribution and are introduced one at a time at random locations as time progresses.

5.1.5.1. NUCLEATION AT **t** = **0** S

The results for random nucleation as initial conditions are shown in Figure 5.9 where a 3D isometric image is shown on the left and a 2D cross-sectional slice at the centre of the domain is shown on the right after the system is allowed to evolve for some time. The 2D slice shows a polygranular structure with columnar and equiaxed grains. While this method might be useful for some limited testing cases, it is difficult to justify this method for a CVD model since it is unrealistic for a large number of grains to nucleate all at once in a given volume ahead of the growing SiC interface.



Figure 5.7: 3D isometric view.



Figure 5.8: 2D slice through the centre of the domain.

Figure 5.9: Random nucleation as initial conditions.

5.1.5.2. NUCLEATION AT t > 0 S

The results for random nucleation at random time steps are shown in Figure 5.12 where a 3D isometric image is shown on the left and a 2D slice at the centre of the domain is shown on the right after the system is allowed to evolve for some time. This simulation starts with nuclei on the substrate surface as initial conditions and introduces new nuclei randomly as time progresses provided there is a gaseous volume to introduce a solid SiC nucleus in. This means that there will be fewer nuclei overall since, as the existing grains grow, there will be less gaseous volume left to nucleate in. The 2D slice shows columnar grains on the bottom followed by an equiaxed grain above them. This suggests that this method of nucleation is suited for modelling columnar to equiaxed transition modelling granted that the nucleation rate is modelled to have a more representative distribution or it is set to be dependent on temperature.



Figure 5.10: 3D aerial view.



Figure 5.11: 2D slice through the centre of the domain.

5.1.6. QUALITATIVE COMPARISON WITH EXPERIMENT

A simulation was run with predetermined nucleation sites (nucleation at t = 0 s) to capture the polygranular structure of the SiC layer and compare it with an experimental image of the SiC microstructure. Figure 5.13 shows a cross section of the result juxtaposed on top of an EBSD image for qualitative comparison. Here, spherical nuclei were inserted at random locations throughout the volume of the simulation as an initial condition. The grains were given time to evolve to examine the microstructure

Figure 5.12: Random nucleation at random time steps.

produced by the model. The simulation successfully produced a complex microstructure with grains of varied sizes and spatial orientations. With the qualitative similarities between the simulation results and the experimental images, the results show that the model can be used to produce SiC microstructure to inform experiments.



Figure 5.13: EBSD image of the TRISO SiC layer between IPyC below and OPyC above obtained by the Canadian Nuclear Laboratories. A cross-section of a phase field simulation result is juxtaposed for qualitative comparison.

5.1.7. LARGER SCALE SIMULATIONS

Larger scale simulations were run in a simulated volume that was 8 times as large as the previous testing model with 100 initial nuclei (Figure 5.14) to test the performance of the model and the capability to produce the polygranular microstructure seen in the EBSD image above. The capability of the model to simulate a large number of growing nuclei at a larger scale, and producing a microstructure resembling the experimental EBSD image further highlights the ability of the model to produce results at experimentally relevant scales, aided significantly by the use of the GM solver.



Figure 5.14: Simulation results showing isometric view (left column) and the morphology on the substrate (right column) with 100 initial nuclei. The stages of growth are a & e) time = 0 s showing an empty domain followed by b & f) time = 0.010 s and c & g) time = 0.042 s, and d & h) time = 0.075 s showing growth.

The simulation results conform to Volmer-Weber growth from Figure 2.5 in the first stage, subfigures (a, e), until the nuclei meet in subfigures (b,f), followed by columnar growth in (c-d, g-h) (see Figures 5.1, 5.3, and 5.14). Discrete nucleation at random time steps could potentially be used to capture columnar to equiaxed grain transition. However, the lack of a temperature dependent nucleation rate does raise the issue of the reliability of the results. Therefore, for the purpose of this work, nucleation at t > 0 s is adopted as the method of choice for nucleation and the implementation of columnar to equiaxed transition, while keeping in mind that it is not the final iteration of the algorithm. To address this issue, the model must either include heat transfer to track the constitutional undercooling of the gaseous phase ahead of the growing interface to trigger nucleation, or implement a temperature dependent nucleation rate.

5.2. SIC CVD RESULTS

Having developed and tested the phase field model of CVD growth as described in section 5.1, the model is then used with material properties obtained from the literature, as outlined in section 4.4, to simulate the growth of SiC by CVD. To test the model as applied to the SiC CVD system, a set of benchmark simulations were run at varied temperatures and precursor gas ratios (analogous to varied concentration of gases) to calculate the deposition rate, a measurable value to compare with experiments. Then a larger scale simulation was run including random nucleation at t > 0 s as described above, to observe the microstructure produced with the real material properties.

5.2.1. PRECURSOR GAS RATIO DEPENDENT DEPOSITION RATE

Using the material properties, isothermal and isobaric simulations were run at different temperatures and concentrations of the precursor gases. All simulations were run at a pressure of 1 atm in a 100 μ m × 100 μ m × 100 μ m domain. This was achieved by varying the number of mols of the H₂ gas while keeping the amount of MTS at 1 mol, therefore varying the ratio of MTS:H₂. The ratio of H₂:Ar was kept 1:1 for all simulations. The molar fraction from the FactSage Equilib calculations were used as described in section 4.3. The growth rate was calculated in m/s then converted to units of mg/cm²min, and the x-axis was set to the product of the partial pressure of MTS to the square root of the partial pressure of H₂, to match Figure 3.3 from the literature for comparison. The results in Figure 5.15 show the trend of faster deposition rate at higher H_2 concentration, as well as overall higher deposition rate at higher temperatures. Both of these trends agree with the experimental results reported in the literature and shown in Figures 3.2 and 3.3. However, when examining the growth rates in the figure, the current results disagree with the literature values by one order of magnitude, suggesting that some of the parameters should be tuned to better match the reported results. Other reasons for the inaccuracy include the unrealistic flat shape of the substrate surface, lack of curvature on the grain surface, having a single grain orientation and no effects from multiphase interfacial energies, and effects from the Dirichlet boundary conditions. More importantly, the model relies on diffusion alone to transport the gaseous species from the Dirichlet boundary condition and does not include convection in the formulation. The reason for using the current parameters is that they were in the literature as mentioned in section 4.4. Nevertheless, this shows that the current model is capable of simulating the 3D microstructure of SiC with real material properties and produce reasonable results, with the correct trends as precursor gas concentration and temperature is varied.



Figure 5.15: SiC layer growth rate at varied ratios between the precursor gases for different temperature. The points represent the data obtained from the simulations and the dashed lines are linear fits of the data.

Figure 5.16 shows the simulation geometry used for the growth rate calculations. All simulations start with an initial condition of a grid of spherical nuclei, intended to approximate a bumpy flat growing SiC interface. The integrals of the field variable, i.e. volume fraction of the phases, were plotted

over time as shown in Figure 5.18. The plot shows that the total solid fraction increases uniformly until it occupies the entire volume of the simulation domain. Figure 5.17 shows the phase and concentration of SiC And Ar in the z-direction at the same time steps as Figure 5.16, the concentration values are normalized to the maximum concentration of SiC in the solid phase. The figure shows the growth of the solid interface as expected.



Figure 5.16: Simulation used to obtain growth rate data. (a & e) t = 0 s, (b & f) t = 144.497 s, (c & g) t = 640.257 s, and (d & h) t = 2026.63 s.


Figure 5.17: A plot of parameters values over a line extending from the bottom to the top of the simulation domain. The snapshots correspond to the simulation of the growth rate stages: (a) Initial condition snapshot at t = 0 s, (b) t = 19.0481 s, (c) t = 57.0481 s, and (d) t = 85.3058 s.

5.2.2. POLYGRANULAR SIC GROWTH BY CVD

The model with the material properties outlined in section 4.4 was used again to run a large scale simulation at a scale of $1000 \,\mu\text{m} \times 1000 \,\mu\text{m} \times 1000 \,\mu\text{m}$ including nuclei on the substrate as an initial conditions as well as random nucleation above the substrate. The results shown in Figure 5.19 show hundreds of randomly generated nuclei at an experimentally relevant length and time scale. Here, nucleation was set to occur arbitrarily within the first 100 time steps. Given the tight time frame of nucleation, the spherical geometry of the nuclei interface, and the proximity of the nuclei to the top



Figure 5.18: Volume fraction of the solid phase over the length of the simulation at T = 1000°C, MTS:H₂ = 1:1. ϕ_{total} is the phase field variable of the solid phases.

surface with Dirichlet boundary conditions, the nuclei ahead of the substrate surface experience faster growth. On the other hand, the interface curvature, and more grain-grain boundaries in the nuclei at the bottom surface result in slower growth in those grains. These factors cause the discrepancy in growth rates seen in Figure 5.19. This could be solved with more sparse nucleation times, or staggering nucleation locations starting closer to the bottom of the volume and nucleation at higher heights at later time steps. Overall, these results highlight the success in achieving experimentally relevant length and time scales, simulating a statistically significant number of grains while including real material properties, thermodynamic driving forces informed by CALPHAD, and concurrent nucleation and coarsening. Moreover, this was achieved on a desktop workstation with a wall clock time of less than a day (typically an overnight simulation).



Figure 5.19: Polygranular SiC deposition by CVD. Aerial view from two different angles at 4 time steps. (a) Initial conditions with hundreds of nuclei on the bottom surface (b) random nucleation ahead of the interface (c) and (d) growth, with the final time step at t = 3000 s.

5.3. PERFORMANCE COMPARISONS

To highlight the impact of the GM solver, partially enabled by the simplified form of the quadratic potential, a performance benchmark was run on a workstation with a 24 core CPU and 256 GB of RAM for 10 time steps and recorded the walltime and peak memory usage while varying the degrees of freedom (DoF)s of the simulations. The results are shown in Figures 5.20 and 5.21 where the dots are the data points and the curves are the lines of best fit. The equations for the best fit lines are summarized in Table 5.1. A Python script was used to measure the walltime of executing the command that runs the simulations which is affected by all the other processes running on the machine. The memory was measured by the built-in memory profiler, resulting in more accurate data than the walltime measurements.



Figure 5.20: Walltime as a function of degrees of freedom comparison between direct and GM solver. The top figure shows the results from both solver while the lower figure shows only the direct solver data for a clearer, magnified view.



Figure 5.21: Memory usage as a function of degrees of freedom comparison between direct and GM solver. The top figure shows the results from both solver while the lower figure shows only the direct solver data for a clearer, magnified view.

The first thing to notice is the lack of data-points for the direct solver compared to the GM solver. This was due to the fact that the direct solver cannot handle such large systems when compared to the GM solver, and attempting to obtain data for higher DoFs with the direct solver was unfeasible. The direct solver is unsuitable for two reasons: either the time to solve the system becomes unreasonably long, or the solver fails altogether due to the fact that the direct solver keeps the entire linear system (the matrix) in the memory. In contrast, the GM solver divides the matrix into smaller matrices, meaning that a larger system with high DoFs will overload the RAM much earlier than a GM solver would. This shows the value of using the GM solver, aided by the quadratic approximation of the potentials, in enabling the simulation of systems with higher DoFs that are more experimentally relevant.

Theoretically, the sparse direct solver scales approximately as $\mathcal{O}(n^2)$. A curve of best fit was fitted

Table 5.1: Scaling trends of walltin	ne and peak memo	ry usage for the o	direct and GM	í solvers, whe	ere y represents th	e
param	eter in the column	title, and n is the	number of De	oFs.		

	Walltime	Memory		
Direct solver	$y = 10.8n^{1.6}$	$y = 52.5n^2 + 12.9$		
GM solver	$y = 0.01n^{1.59}$	y = 4.3n + 7.4		

to the data points and shown in blue in Figure 5.20. The scaling of GM solvers could depend on factors such as the number of levels and the type of cycle used, but it typically scales as $\mathcal{O}(n)$. Here, the line of best fit shown in orange in Figure 5.20, suggesting that other processes in the code may be increasing the computational expense over linear trend. However, it is much more likely that the increased time is a result of the timing method used. Regardless of the scaling captured here, it is evident that there is a substantial difference in the processing time between the solvers. The value of the GM solver is further highlighted by its ability to solve a system with $\approx 5 \times 10^7$ DoFs on a regular desktop computer.

Examining the peak memory usage, sparse direct solver scales as $\mathcal{O}(n^2)$ as expected, shown by the line of best fit in blue in Figure 5.21. Similarly, the GM solver scales linearly as expected as shown by the best-fit line in Figure 5.21 in orange.

6

CONCLUSION

The effort of developing a phase field modelling capability for the SiC TRISO layer deposition process was documented in this report starting with the importance of understanding and controlling the microstructure of the SiC layer from a reactor safety perspective, introducing phase field modelling and summarizing related work in the literature along with their shortfalls and the challenges associated with developing a desired model. The development of a thermodynamically informed phase field model was documented in the methodology chapter followed by the results from multiple evolutionary simulations. The advances made in the current effort are listed in the discussion section followed by recommendations for future work.

To develop an experimentally relevant model, the effort started by deriving the quadratic composite function to enable a CALPHAD informed model that is compatible with the GM iterative solver. The computationally efficient GM solver enabled the simulation of experimentally relevant scales in 3D, on a desktop workstation in a reasonable amount of time (6 to 35 hours of wall clock time). The model incorporates density variation between phases based on recent work from the literature, allowing for multiphase implementation with composition-dependent elastic response and densification.

The model successfully captures nucleation and columnar growth of grains. Decomposition was

tested as a proxy to nucleation to evaluate whether it can capture columnar to equiaxed growth transition. Despite nucleating equiaxed grains ahead of the interface, it was an unsatisfactory method due to the nucleation of the same grains ahead of the interface, which results in the grains combining into one larger columnar grain, and in some cases growing from the top (Dirichlet boundary condition) to the bottom.

Nucleation was implemented in a few different methods: ICs only, randomized nucleation starting with an empty domain, and randomized nucleation starting with ICs of a SiC substrate. ICs only meant starting with a preexisting SiC substrate and letting it grow, while randomized nucleation was achieved by populating arrays for nucleation time-step, location, and phase type (grain orientation) sampled from a uniform distribution and providing those arrays as hard-coded inputs to the simulation. Randomized nucleation showed promising results as a method to simulate equiaxed gain growth ahead of a columnar growing front, as well as providing a robust method to implement nucleation with a nucleation rate that is dependent on other parameters (e.g., temperature) in future work.

After the model was developed and tested, it was used to model the deposition of SiC by CVD. This was achieved by using material properties obtained from the literature as the parameters used in the simulation. The model was compared against experimental results reported in the literature. In terms of quantitative results, a benchmark simulation was set up with a single solid and it was run at varied temperatures and precursor gas ratio (namely, MTS:H₂). These simulations were used to calculated the deposition rate of the SiC layer and the trends agreed with the results reported in the literature. That is, the deposition rate increases with increasing temperatures and increased hydrogen gas concentrations.

Then, using the material properties and including random nucleation, a large scale simulation was run to test the capability of modelling the microstructure evolution of the SiC layer during CVD. This simulation achieved experimentally relevant length and time scales $(1000 \,\mu\text{m} \times 1000 \,\mu\text{m}$ volume, and ≈ 50 minutes), statistically significant number of solid grains (hundreds of nuclei on the substrate surface as initial conditions and nucleation events above the growing interface) and 3D geometry, while also being manageable on a desktop workstation with reasonable execution time (on the order of several hours).

The model was capable of simulating experimentally relevant length and time scales and capture

microstructural evolution as well as the correct trends in growth rate with varied input parameters. However, further work is required to match experimental results in both layer deposition rate and accurate microstructures before the model is validated and can be used to inform the manufacturing process for TRISO fuel.

Since that the primary objective of this work was developing the modelling capability to predict and understand the microstructure of the TRISO layers and the relationship with the fluidized bed parameters to inform the experimentalists and support safety cases, a considerable number of advancements have been made in this effort. The advancements in this thesis are further highlighted when compared to models in the literature which are often only 2-dimensional, rely on idealized models and rarely incorporate real material properties, provide limited value to the experimentalists, and require a significant amount of computational resources to run.

7

RECOMMENDATION FOR FUTURE WORK

Having investigated all the components of the model to be implemented, some weaknesses were identified. To address the shortcoming of this project, future work should pursue the following avenues.

One of the major setbacks in this work was the lack of an adequate nucleation model, which is a common problem in the phase field community. Therefore, it is extremely valuable to pursue the development of a nucleation method that is temperature dependent. As an initial step, it might be worth to explore modifying the current predetermined randomly generated nucleation method by sampling from a different type of distribution, as opposed to the currently used uniform distribution. This could mean populating the predetermined arrays by statistics based on CNT, or perhaps other statistical physics-informed distributions.

On the other hand, it is worthwhile to implement heat transport in the model. This would allow to track the constitutional undercooling ahead of the growing SiC interface, which would trigger nucleation in a more natural form, and capture columnar-to-equixaed transition as reported in the literature.

The next valuable pursuit would be to directly collaborate with experimentalist and validate the model against FB-CVD or spouted bed CVD data. This can be achieved by reproducing repeated exper-

iments such as the growth rate measurements, and the microstructure of the SiC layer. Once the model is validate and deemed capable of producing reliable microstructure morphology, then the model can be used to inform future experiments and TRISO manufacturing process.

Other relevant improvements on the model could include further investigation into orientation implementations and methods to introduce mis-orientation dependent interfacial energy, nucleus morphology and orientation during nucleation, and deployment on high performance computing platforms to simulate systems with higher DoFs.

Some minor software development tasks could help improve the model and make it more user friendly while avoiding errors. These include implementing temperature dependent material properties within the code such that the user only needs to provide the temperature of the system. Similarly, the function use to call and build the thermodynamic potentials should also accept the temperature and the molar ratio of the precursor gases as an input. This would result in having a single script that runs the simulation, and the temperature of the system only needs to be defined in one place. One final task would be to find a method to write vectors of more than three elements, which is a particular restriction in Firedrake. The truncation of the output vector limits the number of grain orientation (phases) that can be visualized.

Together, these developments will enable the model to simulate larger systems with more realistic grain distributions. The model could provide insight into the relationship between fluidized bed parameters and resulting microstructure. It may apply to optimizing particle properties, design of large-scale production lines, and quality control of the manufacturing process. The completed model can also be used to study other CVD systems as well as chemical vapour infiltration (CVI) systems, the latter being of interest to study the deposition of SiC into the porous IPyC and the effects on the IPyC-SiC interface strength.

65

REFERENCES

- [1] International Atomic Energy Agency, "Advances in high temperature gas cooled reactor fuel technology," tech. rep., Vienna, Austria, 2013.
- [2] Nuclear Eenergy Agency, "The NEA small modular reactor dashboard: Second edition," Tech. Rep. 7671, Paris, France, 2024.
- [3] N. Piccinini, "Coated nuclear fuel particles," in *Advances in Nuclear Science and Technology* (E. J. Henley and J. Lewins, eds.), ch. 6, pp. 255–341, Academic Press, 1975.
- [4] United States Nuclear Regulatory Commission and Canadian Nuclear Safety Commission, US-NRC – CNSC Memorandum of Cooperation INTERIM JOINT REPORT 2 concerning Tristructural Isotropic (TRISO) Fuel Qualification. CNSC e-Docs 6779158, US-NRC ML22101A297, 2022.
- [5] M. Liu, R. Liu, B. Liu, and Y. Shao, "Preparation of the Coated Nuclear Fuel Particle Using the Fluidized Bed-chemical Vapor Deposition (FB-CVD) Method," *Procedia Engineering*, vol. 102, pp. 1890–1895, 2015.
- [6] Q. Wu, S. Yu, H. Zhong, X. Li, T. Xiao, L. Liu, X. Guo, Y. Li, and Y. Nie, "Preparation of silicon carbide coating by chemical vapor deposition by using hexamethyldisilylamine precursor," *Surface and Coatings Technology*, vol. 334, pp. 78–83, 2018.
- [7] T. J. Gerczak, R. Seibert, and J. D. Hunn, "Role of microstructure on CO corrosion of SiC layer in UO₂-TRISO fuel," *Journal of Nuclear Materials*, vol. 537, p. 152185, 2020.
- [8] K. Conlon, "Private communication in TRISO Focus Group Meeting," (Chalk River, Ontario, Canada), May 2024.
- [9] N. Moelans, B. Blanpain, and P. Wollants, "An introduction to phase-field modeling of microstructure evolution," *Calphad*, vol. 32, pp. 268–294, 2008.

- [10] M. J. Welland, "Introduction to the phase-field modelling technique: A primer on the Allen-Cahn and Cahn-Hilliard models," in *State-of-the-Art Report on Multi-Scale Modelling Methods*, no. NEA/NSC/R(2019)2, pp. 128–142, Canada: Nuclear Energy Agency (NEA), 2020.
- [11] M. J. Welland, M. H. A. Piro, S. Hibbins, and N. Wang, "A method of integrating CALPHAD data into phase-field models using an approximated minimiser applied to intermetallic layer growth in the Al-Mg system," *Calphad*, vol. 59, pp. 76–83, 2017.
- [12] J. A. Stewart and D. E. Spearot, "Phase-field models for simulating physical vapor deposition and grain evolution of isotropic single-phase polycrystalline thin films," *Computational Materials Science*, vol. 123, pp. 111–120, 2016.
- [13] S. Yang, J. Zhong, M. Chen, and L. Zhang, "A parametric three-dimensional phase-field study of the physical vapor deposition process of metal thin films aiming at quantitative simulations," *Coatings*, vol. 9(10), no. 607, 2019.
- [14] J. A. Stewart and R. Dingreville, "Microstructure morphology and concentration modulation of nanocomposite thin-films during simulated physical vapor deposition," *Acta Materialia*, vol. 188, pp. 181–191, 2020.
- [15] J. A. Stewart, D. L. Damm, R. P. M. Dingreville, and P. K. Hamilton, "Understanding microstructure variability in vapor-deposited energetic materials by using phase-field methods," Tech. Rep. SAND-2020-10255R; 690913, Sandia National Laboratory, Albuquerque, NM (United States), 2020.
- [16] J. A. Stewart and D. E. Spearot, "Physical vapor deposition of multiphase materials with phase nucleation via a coupled phase-field approach," *Computational Materials Science*, vol. 143, pp. 71–79, 2018.
- [17] J. A. Stewart and D. E. Spearot, "Phase-field simulations of microstructure evolution during physical vapor deposition of single-phase thin films," *Computational Materials Science*, vol. 131, pp. 170–177, 2017.
- [18] J. Zhuang, W. Zhao, L. Qiu, J. Xin, J. Dong, and F. Ding, "Morphology evolution of graphene dur-

ing chemical vapor deposition growth: A phase-field theory simulation," *The Journal of Physical Chemistry C*, vol. 123, pp. 9902–9908, 2019.

- [19] M. J. Welland, K. D. Colins, N. Ofori-Opoku, A. A. Prudil, and E. S. Thomas, "Multiscale mesoscale modeling of porosity evolution in oxide fuels," *Journal of Nuclear Engineering and Radiation Science*, vol. 6, no. 1, p. 011105, 2019.
- [20] A. D. Pelton, *Phase Diagrams and Thermodynamic Modeling of Solutions*. Amsterdam: Elsevier, 2019.
- [21] M. Hillert, Phase Equilibria, Phase Diagrams and Phase Transformations: Their Thermodynamic Basis. Cambridge: Cambridge University Press, 2 ed., 2007.
- [22] M. Piro, S. Simunovic, T. Besmann, B. Lewis, and W. Thompson, "The thermochemistry library Thermochimica," *Computational Materials Science*, vol. 67, pp. 266–272, 2013.
- [23] U. Kattner, "The CALPHAD method and its role in material and process development," *Tecnologia em Metalurgia, Materiais e Mineracao*, vol. 13, pp. 3–15, 2016.
- [24] P. A. Demkowicz, B. Liu, and J. D. Hunn, "Coated particle fuel: Historical perspectives and current progress," *Journal of Nuclear Materials*, vol. 515, pp. 434–450, 2019.
- [25] P. A. Demkowicz, J. Hunn, and D. W. Marshall, Advanced Gas Reactor Fuel Specification Technical Bases. No. INL/RPT-23-71992-Rev000, 2023. Idaho National Laboratory, Idaho Falls, ID (United States).
- [26] D. Stinton, W. J. Lackey, and R. Spence, "Production of spherical UO₂-UC₂ for nuclear fuel applications using thermochemical principles," *Journal of the American Ceramic Society*, vol. 65, no. 7, pp. 321–324, 1982.
- [27] R. Hunt, J. Collins, M. Lloyd, and S. Finkeldei, "Production of more ideal uranium trioxide microspheres for the sol-gel microsphere pelletization process without the use of carbon," *Journal of Nuclear Materials*, vol. 515, pp. 107–110, 2019.
- [28] R. D. Hunt, T. B. Lindemer, M. Z. Hu, G. D. del Cul, and J. L. Collins, "Preparation of spherical, dense uranium fuel kernels with carbon," *Radiochimica Acta*, vol. 95, no. 4, pp. 225–232, 2007.

- [29] D. W. Marshall, "AGR-5/6/7 fuel fabrication report," Tech. Rep. INL/EXT-19-53720-Rev000, Idaho National Laboratory, Idaho Falls, ID (United States), 2019.
- [30] A. S. H. Makhlouf, "Current and advanced coating technologies for industrial applications," in *Nanocoatings and Ultra-Thin Films* (A. S. H. Makhlouf and I. Tiginyanu, eds.), pp. 3–23, Woodhead Publishing, 2011.
- [31] A. Y. C. Nee, ed., *Handbook of Manufacturing Engineering and Technology*. London: Springer London, 2015.
- [32] C. Morosanu, "Nucleation and growth of CVD films," in *Thin Films by Chemical Vapour Deposition*, Thin Films Science and Technology, pp. 163–176, Amsterdam: Elsevier, 1990.
- [33] L. Sun, G. Yuan, L. Gao, J. Yang, M. Chhowalla, M. H. Gharahcheshmeh, K. K. Gleason, Y. S. Choi,
 B. H. Hong, and Z. Liu, "Chemical vapour deposition," *Nature Reviews Methods Primers*, vol. 1, no. 5, 2021.
- [34] C. Morosanu, "Kinetics of CVD," in *Thin Films by Chemical Vapour Deposition*, Thin Films Science and Technology, pp. 101–140, Amsterdam: Elsevier, 1990.
- [35] G. H. Gilmer, H. Huang, and C. Roland, "Thin film deposition: fundamentals and modeling," *Computational Materials Science*, vol. 12, pp. 354–380, 1998.
- [36] C. Bale, E. Bélisle, P. Chartrand, S. Decterov, G. Eriksson, A. Gheribi, K. Hack, I.-H. Jung, Y.-B. Kang, J. Melançon, A. Pelton, S. Petersen, C. Robelin, J. Sangster, P. Spencer, and M.-A. Van Ende, "FactSage thermochemical software and databases, 2010–2016," *Calphad*, vol. 54, pp. 35–53, 2016.
- [37] J.-O. Andersson, T. Helander, L. Höglund, P. Shi, and B. Sundman, "Thermo-Calc & DICTRA, computational tools for materials science," *Calphad*, vol. 26, pp. 273–312, 2002.
- [38] G. Eriksson and K. Hack, "ChemSage a computer program for the calculation of complex chemical equilibria," *Metallurgical Transactions B*, vol. 21, pp. 1013–1023, 1990.
- [39] C. Guéneau, N. Dupin, L. Kjellqvist, E. Geiger, M. Kurata, S. Gossé, E. Corcoran, A. Quaini, R. Hania, A. Smith, M. Piro, T. Besmann, P. Turchi, J. Dumas, M. Welland, T. Ogata, B. Lee, J. Kennedy,

C. Adkins, M. Bankhead, and D. Costa, "TAF-ID: An international thermodynamic database for nuclear fuels applications," *Calphad*, vol. 72, p. 102212, 2021.

- [40] B. Sundman, U. R. Kattner, C. Sigli, M. Stratmann, R. Le Tellier, M. Palumbo, and S. G. Fries, "The OpenCalphad thermodynamic software interface," *Computational Materials Science*, vol. 125, pp. 188–196, 2016.
- [41] A. Roy, T. Pramanik, S. Chowdhury, and S. K. Banerjee, "Phase-Field Modeling of Chemical Vapor-Deposited 2D MoSe₂ Domains with Varying Morphology for Electronic Devices and Catalytic Applications," ACS Applied Nano Materials, vol. 5, pp. 15488–15497, 2022.
- [42] V. P. Narayana Samy, M. Schäfle, F. Brasche, U. Krupp, and C. Haase, "Understanding the mechanism of columnar–to-equiaxed transition and grain refinement in additively manufactured steel during laser powder bed fusion," *Additive Manufacturing*, vol. 73, p. 103702, 2023.
- [43] M. Price, "The Dragon project origins, achievements and legacies," *Nuclear Engineering and Design*, vol. 251, pp. 60–68, 2012.
- [44] A. C. Kadak, "The status of the US high-temperature gas reactors," *Engineering*, vol. 2, no. 1, pp. 119–123, 2016.
- [45] Z. Zhang, Y. Dong, F. Li, Z. Zhang, H. Wang, X. Huang, H. Li, B. Liu, X. Wu, H. Wang, X. Diao, H. Zhang, and J. Wang, "The Shandong Shidao Bay 200 MWe high-temperature gas-cooled reactor pebble-bed module (HTR-PM) demonstration power plant: An engineering and technological innovation," *Engineering*, vol. 2, no. 1, pp. 112–118, 2016.
- [46] K. Nagatsuka, H. Noguchi, S. Nagasumi, Y. Nomoto, A. Shimizu, H. Sato, T. Nishihara, and N. Sakaba, "Current status of high temperature gas-cooled reactor development in japan," *Nuclear Engineering and Design*, vol. 425, p. 113338, 2024.
- [47] P. J. Pappano, "Xe-100 pebble bed small modular reactor: Solving critical challenges to enable the Xe-100 pebble bed advanced reactor concept (ARC) (final scientific and technical report)," Tech.
 Rep. 1971498, X Energy, LLC, Rockville, MD (United States), 2023.

- [48] J. P. Gorton, R. C. Gallagher, Z. G. Wallen, A. G. Le Coq, G. W. Helmreich, C. M. Petrie, K. D. Linton, R. Latta, and T. J. Gerczak, "Simulation of a triso minifuel irradiation experiment with datainformed uncertainty quantification," *Nuclear Engineering and Design*, vol. 404, p. 112177, 2023.
- [49] A. Le Coq, C. Petrie, J. Harp, T. Gerczak, K. Linton, and R. Latta, "UCO TRISO MiniFuel FY23 NSUFKairos Power Post-Irradiation Examination Status Report," Tech. Rep. ORNL/TM-2023/2985, Oak Ridge National Laboratory, TN, United States, 2023.
- [50] D. Marshall and M. Sharp, "Readiness review of BWXT for fabrication of AGR-5/6/7 TRISO particles," Tech. Rep. INL/EXT-16-37982Rev0, Idaho National Laboratory, Idaho Falls, ID (United States), 2016.
- [51] United States Nuclear Regulatory Commission, "Environmental impact statement for the construction permit for the kairos hermes test reactor," tech. rep., United States Nuclear Regulatory Commission, Office of Nuclear Material Safety and Safeguards, 2023.
- [52] Westinghouse Electric Company, "First canadian eVinci[™] microreactor targeted for Saskatchewan," 2023. https://info.westinghousenuclear.com/news/first-canadian-evincimicroreactor-targeted-for-saskatchewan.
- [53] X-Energy, "X-energy, transalta partner to study deployment of advanced small modular nuclear reactors in alberta through emissions reduction alberta award," 2024. https://xenergy.com/media/news-releases/x-energy-transalta-partner-to-study-deployment-ofadvanced-small-modular-nuclear-reactors-in-alberta-through-emissions-reduction-albertaaward.
- [54] X-Energy, "X-energy successfully completes canadian pre-licensing milestone for the Xe-100 advanced small modular reactor," 2024. https://x-energy.com/media/news-releases/canadian-prelicensing-xe-100-advanced-small-modular-reactor.
- [55] Canadian Nuclear Laboratories, "Cnl successfully fabricates advanced small modular reactor fuel," 2021. https://www.cnl.ca/cnl-successfully-fabricates-advanced-small-modular-reactorfuel/.

- [56] Q. Li, Y. Zhang, B. Ji, S. Zhang, and R. Tu, "Improvement of SiC deposition uniformity in CVD reactor by showerhead with baffle," *Journal of Crystal Growth*, vol. 615, p. 127255, 2023.
- [57] X. Yang, F. Zhang, M. Guo, Y. Zhong, P. Wang, J. Lin, and Z. Zhu, "Preparation of SiC layer with submicro grain structure in TRISO particles by spouted bed CVD," *Journal of the European Ceramic Society*, vol. 39, no. 9, pp. 2839–2845, 2019.
- [58] C. Lu, L. Cheng, C. Zhao, L. Zhang, and Y. Xu, "Kinetics of chemical vapor deposition of SiC from methyltrichlorosilane and hydrogen," *Applied Surface Science*, vol. 255, no. 17, pp. 7495–7499, 2009.
- [59] S. Fashu, J. Yang, L. Yang, and N. Wang, "Phase-field modelling of 2D island growth morphology in chemical vapor deposition," *Eur. Phys. J. E*, vol. 43, no. 57, 2020.
- [60] Y. Huang, S. L. Masters, S. P. Krumdieck, and C. M. Bishop, "Phase field model of faceted anatase TiO₂ dendrites in low pressure chemical vapor deposition," *Applied Physics Letters*, vol. 119, no. 22, p. 221602, 2021.
- [61] M. J. Welland and N. Ofori-Opoku, "Simple method of including density variation in quantitative continuum phase-change models," *Phys. Rev. Lett.*, vol. 128, p. 075701, 2022.
- [62] M. J. Welland and N. Ofori-Opoku, "Introducing density variation and pressure in thermodynamically self-consistent continuum phase-change models including phase-field," *Phys. Rev. Mater.*, vol. 6, p. 043805, 2022.
- [63] M. Welland and S. Hanlon, "Prediction of the zirconium hydride precipitation barrier with an anisotropic 3D phase-field model incorporating bulk thermodynamics and elasticity," *Computational Materials Science*, vol. 171, p. 109266, 2020.
- [64] M. J. Welland, E. Tenuta, and A. A. Prudil, "Linearization-based method for solving a multicomponent diffusion phase-field model with arbitrary solution thermodynamics," *Physical Review E*, vol. 95, 2017.
- [65] A. Ulvestad, M. J. Welland, S. Collins, R. Harder, E. Maxey, J. Wingert, A. Singer, S. Hy, P. Mulvaney,

P. Zapol, and O. G. Shpyrko, "Avalanching strain dynamics during the hydriding phase transformation in individual palladium nanoparticles," *Nature Communications*, vol. 6, no. 10092, 2015.

- [66] A. Ulvestad, M. J. Welland, W. Cha, Y. Liu, J. W. Kim, R. Harder, E. Maxey, J. N. Clark, M. J. Highland, H. You, P. Zapol, S. O. Hruszkewycz, and G. B. Stephenson, "Three-dimensional imaging of dislocation dynamics during the hydriding phase transformation," *Nature Materials*, vol. 16, p. 565–571, 2017.
- [67] M. Piro, M. Welland, and M. Stan, "On the interpretation of chemical potentials computed from equilibrium thermodynamic codes," *Journal of Nuclear Materials*, vol. 464, pp. 48–52, 2015.
- [68] N. Ofori-Opoku, J. A. Warren, and P. W. Voorhees, "Self-consistent modeling of anisotropic interfaces and missing orientations: Derivation from phase-field crystal," *Physical Review Materials*, vol. 2, no. 8, 2018.
- [69] E. J. Munoz, V. Attari, M. C. Martinez, M. B. Dickerson, M. Radovic, and R. Arroyave, "Phase-field model of silicon carbide growth during isothermal condition," *Computational Materials Science*, vol. 242, p. 113058, 2024.
- [70] T. W. Heo and L.-Q. Chen, "Phase-field modeling of nucleation in solid-state phase transformations," *JOM*, vol. 66, no. 8, pp. 1520–1528, 2014.
- [71] S. Karthika, T. K. Radhakrishnan, and P. Kalaichelvi, "A review of classical and nonclassical nucleation theories," *Crystal Growth & Design*, vol. 16, no. 11, pp. 6663–6681, 2016.
- [72] D. Tourret, H. Liu, and J. LLorca, "Phase-field modeling of microstructure evolution: Recent applications, perspectives and challenges," *Progress in Materials Science*, vol. 123, p. 100810, 2022.
- [73] W. Wu, D. Montiel, J. Guyer, P. Voorhees, J. Warren, D. Wheeler, L. Gránásy, T. Pusztai, and
 O. Heinonen, "Phase field benchmark problems for nucleation," *Computational Materials Science*, vol. 193, p. 110371, 2021.
- [74] L. Gránásy, T. Pusztai, D. Saylor, and J. A. Warren, "Phase field theory of heterogeneous crystal nucleation," *Physical Review Letters*, vol. 98, p. 035703, 2007.

- [75] A. Jokisaari, C. Permann, and K. Thornton, "A nucleation algorithm for the coupled conserved–nonconserved phase field model," *Computational Materials Science*, vol. 112, pp. 128–138, 2016.
- [76] H. Butt, K. Graf, and M. Kappl, *Physics and Chemistry of Interfaces*. United States: Wiley, 2003.
- [77] M. Welland and G. Karagozian, "A generalized approach to CALPHAD-informed multiphysics phase-field modelling and efficient quadratic implementatio.," in OECD NEA MMSNF Workshop, (Hamilton, Ontario), 2023.
- [78] T. Kimoto and J. A. Cooper, *Fundamentals of Silicon Carbide Technology: Growth, Characterization, Devices, and Applications.* Singapore: Wiley, 2014.
- [79] A. I. Kingon, L. J. Lutz, P. Liaw, and R. F. Davis, "Thermodynamic calculations for the chemical vapor deposition of silicon carbide," *Journal of the American Ceramic Society*, vol. 66, pp. 558– 566, 1983.
- [80] R. G. Munro, "Material properties of a sintered α-SiC," *Journal of Physical and Chemical Reference Data*, vol. 26, no. 5, pp. 1195–1203, 1997.
- [81] Z. C. Feng, ed., Handbook of Silicon Carbide Materials and Devices. United States: Routledge & CRC Press, 2023.
- [82] P. Nikolopoulos, G. Ondracek, and D. Sotiropoulou, "Wettability and interfacial energies between zirconia ceramic and liquid metals," *Ceramics International*, vol. 15, no. 4, pp. 201–206, 1989.
- [83] T. Pinomaa, N. Ofori-Opoku, A. Laukkanen, and N. Provatas, "Quantitative phase field simulations of polycrystalline solidification using a vector order parameter," *Physical Review E*, vol. 103, p. 053310, 2021.
- [84] M. Yang, L. Wang, and W. Yan, "Phase-field modeling of grain evolution in additive manufacturing with addition of reinforcing particles," *Additive Manufacturing*, vol. 47, p. 102286, 2021.
- [85] D. A. Ham, P. H. J. Kelly, L. Mitchell, C. J. Cotter, R. C. Kirby, K. Sagiyama, N. Bouziani, S. Vorderwuelbecke, T. J. Gregory, J. Betteridge, D. R. Shapero, R. W. Nixon-Hill, C. J. Ward, P. E. Farrell, P. D.

Brubeck, I. Marsden, T. H. Gibson, M. Homolya, T. Sun, A. T. T. McRae, F. Luporini, A. Gregory, M. Lange, S. W. Funke, F. Rathgeber, G.-T. Bercea, and G. R. Markall, *Firedrake User Manual*, first edition ed., 2023.

[86] J. P. Ahrens, B. Geveci, and C. Law, "ParaView: An end-user tool for large-data visualization," in *Visualization Handbook*, pp. 717–731, 2005.

A

FACTSAGE EQUILIB RESULTS

FactSage

8.0

H2 + CH3SiCl3 + Ar =

4.4835 mol gas_ideal

(166.03 gram, 4.4835 mol, 468.40 litre, 3.5446E-04 gram.cm-3)

(1000 C, 1 atm, a=1.0000)

- (0.44014 H2 + 0.22304 Ar
- + 0.21921 HCl
- + 0.10330 SiCl4
- + 8.3183E-03 SiHCl3

- + 3.3742E-03 SiCl3
- + 1.8051E-03 CH4
- + 7.2228E–04 SiCl2
- + 9.2765E-05 SiH2Cl2
- + 4.7147E-07 H
- + 3.0715E-07 C2H4
- + 2.8871E–07 SiH3Cl
- + 2.8215E–07 SiCH3Cl3
- + 2.3539E-07 CH3Cl
- + 1.9926E-07 Cl
- + 1.9291E-07 C2H2
- + 4.4888E-08 CH3
- + 1.0224E-08 C2H6
- + 4.2527E–10 Cl2
- + 3.7444E–10 SiH4
- + 1.0827E–10 SiCl
- + 7.7925E–11 CH2CHCl
- + 3.9483E–11 CH2Cl
- + 1.7306E–11 C2HCl
- + 1.1970E-11 CH2Cl2
- + 9.1925E-12 C2H5
- + 8.2882E–12 C2H5Cl
- + 3.0070E-12 C2H3
- + 2.9625E–13 SiH
- + 1.1033E-13 C2H
- + 4.5983E-14 Si
- + 3.9398E-14 CH2
- + 2.9785E-14 CHCl2
- + 6.9797E-15 C2H2Cl2(g2)

Т

Т

Т

+ 6.4524E-15	C2H2Cl2(g3)	
+ 1.3778E-15	C2H2Cl2(g)	Т
+ 1.8624E-16	C2Cl2	
+ 1.4091E-16	CHCl3	
+ 1.0042E-16	CHCl	
+ 3.6690E-17	CH3CHCl2	Т
+ 1.2809E-17	Si2C	
+ 6.5909E-18	CCl2	
+ 6.3984E-18	SiC2	
+ 1.1520E-18	CHClCCl2	
+ 2.0497E-19	CH	
+ 2.0230E-19	Si2H6	
+ 9.4441E-20	Si2	
+ 3.6647E-20	CCl3	
+ 2.4220E-20	CCl	
+ 5.5065E-21	C2Cl	
+ 1.5010E-21	CHCl2CH2Cl	Т
+ 5.9731E-22	С	
+ 2.0831E-22	CCl4	
+ 4.7602E-23	C3	
+ 4.2695E-23	SiC	
+ 4.1441E-23	Si3	
+ 2.6564E-23	C2Cl3	
+ 1.4876E-24	C2Cl4	
+ 5.7448E-25	C2	
+ 1.5864E-26	CHCl2CHCl2	Т
+ 1.5082E-29	C5	
+ 1.1308E-29	C4	
+ 2.0256E-31	C2Cl5H	Т

+	4.0199E-34	C2Cl5

+ 2.9801E-37 C2Cl6

+ 2.5102E-40 C6Cl6 T)

+ 0.51113 mol C_Graphite (6.1391 gram, 0.51113 mol) (1000 C, 1 atm, S1, a=1.0000)

+ 0.48077 mol SiC_Solid_Beta (19.277 gram, 0.48077 mol) (1000 C, 1 atm, S2, a=1.0000)

Show only stable phases option in effect Cut-off limit for gaseous fractions = 1.00E-75

Data on 9 product species identified with "T" have been extrapolated outside their valid temperature ranges

Η G V S Ср (J) (J) (litre) (J/K) (J/K) * * * * * * * * * * * * * * * * G S Η Ср (J) (J) (J/K) (J/K)gas_ideal -2.64499E+05 -1.60382E+06 1.05197E+03

3.53903E+02		
C_Graphite	9.15928E+03 -1.02734E+04	1.52635E+01
1.18109E+01		
SiC_Solid_Beta	-1.47096E+04 -6.13563E+04	3.66388E+01
2.43613E+01		
Total mass/gram = 191.44		
Total mass/gram excluding gas_ideal	= 25.416	
Databases: FactPS 8.0		
Data Search options: exclude gas io	ns; organic CxHy X(max) =	= 2; min soln
cpts = 2		
Final conditions: $T(C) = 1000$, $P(atr$	m) = 1	

FactSage

8.0

T = 1000 C P = 1 atmV = 468.40 dm3

STREAM CONSTITUENTS	AMOUNT/mol
H2	1.0000E+00
CH3SiCl3	1.0000E+00

Ar

1.0000E+00

		EQUIL AMOUNI	MOLE FRACTION	FUGACITY
PHASE: gas_	_ideal	mol		atm
H2		1.9733E+00	4.4014E-01	4.4014E-01
Ar		1.0000E+00	2.2304E-01	2.2304E-01
HCl		9.8281E-01	2.1921E-01	2.1921E-01
SiCl4		4.6315E-01	1.0330E-01	1.0330E-01
SiHCl3		3.7295E-02	8.3183E-03	8.3183E-03
SiCl3		1.5128E-02	3.3742E-03	3.3742E-03
CH4		8.0932E-03	1.8051E-03	1.8051E-03
SiCl2		3.2383E-03	7.2228E-04	7.2228E-04
SiH2Cl2		4.1591E-04	9.2765E-05	9.2765E-05
Н		2.1138E-06	4.7147E-07	4.7147E-07
C2H4		1.3771E-06	3.0715E-07	3.0715E-07
SiH3Cl		1.2944E-06	2.8871E-07	2.8871E-07
SiCH3Cl3		1.2650E-06	2.8215E-07	2.8215E-07
CH3Cl		1.0554E-06	2.3539E-07	2.3539E-07
Cl		8.9336E-07	1.9926E-07	1.9926E-07
C2H2		8.6491E-07	1.9291E-07	1.9291E-07
CH3		2.0125E-07	4.4888E-08	4.4888E-08
C2H6]	4.5837E-08	1.0224E-08	1.0224E-08
Cl2		1.9067E-09	4.2527E-10	4.2527E-10
SiH4		1.6788E-09	3.7444E-10	3.7444E-10
SiCl		4.8543E-10	1.0827E-10	1.0827E-10
CH2CHCl]	3.4938E-10	7.7925E-11	7.7925E-11
CH2Cl		1.7702E-10	3.9483E-11	3.9483E-11
C2HCl		7.7590E-11	1.7306E-11	1.7306E-11
CH2Cl2		5.3668E-11	1.1970E-11	1.1970E-11

C2H5		4.1214E-11	9.1925E-12	9.1925E-12
C2H5Cl	Т	3.7160E-11	8.2882E-12	8.2882E-12
C2H3		1.3482E-11	3.0070E-12	3.0070E-12
SiH		1.3282E-12	2.9625E-13	2.9625E-13
C2H		4.9468E-13	1.1033E-13	1.1033E-13
Si		2.0617E-13	4.5983E-14	4.5983E-14
CH2		1.7664E-13	3.9398E-14	3.9398E-14
CHCl2		1.3354E-13	2.9785E-14	2.9785E-14
C2H2Cl2(g2)		3.1293E-14	6.9797E-15	6.9797E-15
C2H2Cl2(g3)		2.8929E-14	6.4524E-15	6.4524E-15
C2H2Cl2(g)	Т	6.1771E-15	1.3778E-15	1.3778E-15
C2Cl2		8.3499E-16	1.8624E-16	1.8624E-16
CHCl3		6.3176E-16	1.4091E-16	1.4091E-16
CHCl		4.5021E-16	1.0042E-16	1.0042E-16
CH3CHCl2	Т	1.6450E-16	3.6690E-17	3.6690E-17
Si2C		5.7428E-17	1.2809E-17	1.2809E-17
CCl2		2.9550E-17	6.5909E-18	6.5909E-18
SiC2		2.8687E-17	6.3984E-18	6.3984E-18
CHClCCl2		5.1649E-18	1.1520E-18	1.1520E-18
CH		9.1899E-19	2.0497E-19	2.0497E-19
Si2H6		9.0701E-19	2.0230E-19	2.0230E-19
Si2		4.2342E-19	9.4441E-20	9.4441E-20
CCl3		1.6431E-19	3.6647E-20	3.6647E-20
CCl		1.0859E-19	2.4220E-20	2.4220E-20
C2Cl		2.4688E-20	5.5065E-21	5.5065E-21
CHCl2CH2Cl	Т	6.7296E-21	1.5010E-21	1.5010E-21
С		2.6780E-21	5.9731E-22	5.9731E-22
CCl4		9.3394E-22	2.0831E-22	2.0831E-22
C3		2.1342E-22	4.7602E-23	4.7602E-23

SiC		1.9142E-22	4.2695E-23	4.2695E-23	
Si3		1.8580E-22	4.1441E-23	4.1441E-23	
C2Cl3		1.1910E-22	2.6564E-23	2.6564E-23	
C2Cl4		6.6698E-24	1.4876E-24	1.4876E-24	
C2		2.5757E-24	5.7448E-25	5.7448E-25	
CHCl2CHCl2	Т	7.1127E-26	1.5864E-26	1.5864E-26	
C5		6.7620E-29	1.5082E-29	1.5082E-29	
C4		5.0701E-29	1.1308E-29	1.1308E-29	
C2Cl5H	Т	9.0818E-31	2.0256E-31	2.0256E-31	
C2Cl5		1.8023E-33	4.0199E-34	4.0199E-34	
C2Cl6		1.3361E-36	2.9801E-37	2.9801E-37	
C6Cl6	Т	1.1254E-39	2.5102E-40	2.5102E-40	
TOTAL:		4.4835E+00	1.0000E+00	1.0000E+00	
System component		Amount/mol	Amount/gram	Mole fraction	Mass
fraction					
Ar		1.0000	39.948	0.10496	
0.24061					
Cl		3.0000	106.36	0.31488	
0.64061					
Si		0.51923	14.583	5.4499E-02	
8.7835E-02					
С		8.1003E-03	9.7290E-02	8.5021E-04	
5.8599E-04					
Н		5.0000	5.0397	0.52481	
3.0355E-02					
		mol		ACTIVITY	
C_Graphite(s)		5.1113E-01		1.0000E+00	
SiC_Solid_Beta(s2)		4.8077E-01		1.0000E+00	
* * * * * * * * * * * * * * * * * * * *	* * * * * *	* * * * * * * * * * * * * * *	* * * * * * * * * * * * * * * *	* * * * * * * * * * * *	

Ср	Н	S		G	V	
J.K-1	J	J.K-2	J		dm3	
* * * * * * * * * * * * * * * *	* * * * * * * * * * * * * * *	* * * * * * * * * *	* * * * * * * * * *	* * * * * * * * * *	* * * * * * * * * *	* * * *
3.90075E+02	-2.70049E+05	1.103881	E+03 -1.6	7545E+06	4.683971	E+02
		Ср	Н		S	G
		J.K-1	J	J	K-1	J
gas_ideal	3.	53903E+02	-2.64499E	+05 1.051	97E+03 –	1.60382E+06
C_Graphite(s)	1.	18109E+01	9.15928E	+03 1.526	35E+01 –	1.02734E+04
SiC_Solid_Beta	a(s2) 2.4	43613E+01	-1.47096E	+04 3.663	88E+01 -	6.13563E+04

Show only stable phases option in effect Cut-off limit for gaseous fractions = 1.00E-75

Data on 9 product species identified with "T" have been extrapolated outside their valid temperature ranges

Databases: FactPS 8.0

Data Search options: exclude gas ions; organic CxHy.. X(max) = 2; min soln cpts = 2

Final conditions: T(C) = 1000, P(atm) = 1

B

PYTHON CODE

This chapter includes all the original work contributed by the author. However, there is a large amount of back-end code needed to run the simulations. The code files are shown in sections with the title describing their function. The files include the phase field CVD model code, followed by the file used to setup the Gibbs energies and the Helmholtz energy (again, this file would be an input to a back-end file that builds the thermodynamic potentials). Then, the "tools" library which includes the nucleation algorithm contributed by the author, and finally the script used to generate the random nucleation time step, coordinates, and phase (grain orientaiton).

B.1. PHASE FIELD CVD CODE

from firedrake import *
from tools2 import *
from thermo_potentials import load_potential
from math import log, ceil, comb
from timeit import default_timer as timer

```
# ~~~ Material properties ~~~ #
M_phi = 1e-6#1e-6
T = 1773
RT = 8.314*T
interfacial_energy_SiCAr = 2.24 #J/m^2
interfacial_energy_SiCSiC = .1
interface_width = 5e-6 #m
D = 1.19e-3 #m^2/s - Self diffusion of Ar at latm, 1600 K
potential = load_potential('CVD_4phase_pot') # Thermodynamic potential
```

n = 2 # number of species m = 4 # number of phases

```
# ~~~ Scaling ~~~ #
x_scale = 1e-4
#c_scale = as_vector([89581, 7]) # Typical values of concentration vectors
c_scale = as_vector([89581, 89581]) # Typical values of concentration vectors
```

def gr(x):

return grad(x)/x_scale

~~~ Mesh ~~~
Lx = 1e-3
Ly = Lx
Lz = Lx

Lx_scale, Ly_scale, Lz_scale = Lx/x_scale, Ly/x_scale, Lz/x_scale
interface_width_scale = interface_width/x_scale

```
# Coarse mesh should have an 'appreciable' resolution. Fine mesh is scale of
feature of interest
mesh_res_coarse = Lx_scale/4
mesh_res_final = interface_width_scale*2 #target mesh resolution
mg_levels = ceil( log(mesh_res_coarse/mesh_res_final,2) )
print('Using_{}_levels_of_refinement'.format(mg_levels))
```

hierarchy = MeshHierarchy(mesh, mg_levels)
mesh = hierarchy[-1]

x_mesh = SpatialCoordinate(mesh)

V_phase = VectorFunctionSpace(mesh, "CG", 1, dim = m-1, name="phases")
V_species = VectorFunctionSpace(mesh, "CG", 1, dim=n, name ="species")
V = MixedFunctionSpace([V_species, V_phase])

U = Function(V) dU = TrialFunction(V) test_U = TestFunction(V) test_c, test_phase = split(test_U)

```
c_mesh, phase = split(U)
```

x = x_mesh*x_scale
c = elem_mult(c_mesh, c_scale)

```
#Assemble full vector of phi and p_phase
phi = list(phase)+[1-sum(phase)]
p_phase = [p**3*(6*p**2-15*p+10) for p in phi]
ps = as_vector(p_phase)
```

```
# Build multiphase energy -> to be moved to thermo potential.
```

```
def multiphase(p, interface_width):
```

```
def antisymmetric_gradient(pa, pb):
```

```
return \ 3*(interface\_width**2*(\ pa*gr(pb) \ - \ pb*gr(pa) \ )**2 \ + \ pa**2*pb
```

2*(1+50*(pa+pb-1)2))

return [antisymmetric_gradient(p[i], p[j]) for i in range(len(p)) for j in
range(i)]

interface_area = as_vector(multiphase(phi, interface_width))

```
interfacial_energy = as_vector([interfacial_energy_SiCSiC]*3+[
```

```
interfacial_energy_SiCAr]*3)
```

```
interfacial_energy = interfacial_energy/interface_width
```

```
interface_energy = inner(interfacial_energy, interface_area)
#interface_energy = inner(as_vector([interfacial_energy_SiCSiC/interface_width
]*comb(m,2)), as_vector(interface_area))
```

```
response = potential.grad(list(c)+p_phase)
```

```
mu = as_vector(response[:n])
```

```
P = as_vector(response[n:])
```

```
print('Thermodynamic_driver_forces_loaded')
```

 $D = inner(as_vector(phi), as_vector([1e-5,1e-5,1e-5,1e-3]))$

J = -D/RT * gr (mu)

F_diffusion = as_vector([inner(J[i,:], gr(test_c[i])) for i in range(J. ufl_shape[0])])

F_diffusion = elem_div(F_diffusion, c_scale)

build phase field equations
F_phase_bulk = -M_phi*inner(P, derivative(ps, phase, test_phase))*dx
F_phase_interface = -M_phi*derivative(interface_energy, phase, test_phase)*dx
F_phase = F_phase_bulk + 1*F_phase_interface

```
rad = interface_width*2
rad2 = interface_width
rad3 = interface_width*0.5
rad4 = interface_width*9
```

```
al_centres = [[0.25*Lx,0.25*Lx,-0.5*rad],[0.5*Lx,0.5*Lx,-0.5*rad],[0.75*Lx
,0.75*Lx+2.5*rad,-0.5*rad],[0.75*Lx-rad2-3*rad,0.25*Lx+rad,0],
[0.65*Lx,0.645*Lx,-0.5*rad],[0.45*Lx,0.16*Lx,-0.5*rad],[0.35*Lx
,0.4*Lx,0],[0.5*Lx,0.3*Lx,-0.5*rad],
[Lx-3*rad,4.3*rad,-0.5*rad],[6.5,2*rad,0.1*rad],[3,7,-0.5*rad]]]
```

a1 = create_bubble(a1_centres, rad,x, interface_width)

b1 = create_bubble(b1_centres, rad,x, interface_width)

c1 = create_bubble(c1_centres, rad,x, interface_width)

```
p0 = max_values([a1])
p1 = max_values([b1])
p2 = max_values([c1])
```

```
p_{init} = as_{vector([p0, p1, p2])}
```
U.sub(1).interpolate(p_init)

nuc_centres = []
nuc_phases = []

i=0

while True:

centre = nuc_centres[0]

try:

```
philoc = U.sub(1).at(centre[0])
```

except RuntimeError:

philoc = np.inf*np.ones(U.sub(1).ufl_shape)

comm = mpi4py_comm(U.sub(1).function_space().mesh().mpi_comm())

phiglob = np.zeros_like(philoc)

comm. Allreduce (philoc, phiglob, op=pyMPI.MIN)

#check if nucleation site has phi<threshold to avoid nucleating over naother phase and interpolating phi value >1

counter = 0

while True:

if philoc.max() > 2.14e-2: nuc_centres = nuc_centres[1:] centre = nuc_centres[0] counter +=1 else:

break

```
#exit loop after max_nuc_trials failed loops
if counter > 10 or len(nuc_centres) == 1:
```

break

```
nucleus = create_bubble(centre,rad,x,interface_width)
a,b,c=Constant(0),Constant(0),Constant(0)
if nuc_phases[0] == 'a':
    a = nucleus
elif nuc_phases[0] == 'b':
    b = nucleus
else:
    c = nucleus
p0 = max_values([a,U.sub(1)[0]])
p1 = max_values([b,U.sub(1)[1]])
p2 = max_values([c,U.sub(1)[2]])
```

```
p_init = as_vector([p0,p1,p2])
U.sub(1).interpolate(p_init)
nuc_centres = nuc_centres[1:]
nuc_phases = nuc_phases[1:]
i +=1
if len(nuc_centres) == 0:
```

break

Since using a quadratic potential, we can just get initial values from
 expansion point
pt = potential.additional_fields['expansion_point']

```
print(pt)
```

```
super_saturation = 0

ci = as_matrix([
    [pt['c0_a']/pt['V_a'] / c_scale[0],0],
    [pt['c0_b']/pt['V_b'] / c_scale[0],0],
    [pt['c0_c']/pt['V_c']/ c_scale[0],0],
    [(pt['c0_d']/pt['V_d']+super_saturation) / c_scale[0], (pt['c1_d']/pt['V_d'
    ]-super_saturation)/ c_scale[1] ]])
```

```
c_init = dot(ps,ci)
```

```
U.sub(0).interpolate(c_init)
```

```
# Boundary conditions
bcs = [
    DirichletBC(V.sub(1).sub(0), Constant(0), 6),
    DirichletBC(V.sub(1).sub(1), Constant(0), 6),
    DirichletBC(V.sub(1).sub(2), Constant(0), 6),
    DirichletBC(V.sub(0), ci[-1],6),
    ]
```

~~~ Set-up solver and timestepping

```
params = {
```

```
'snes_monitor': None,
'snes_max_it': 30,
'snes_atol': 1e-6,
'snes_stol': 1e-6,
'snes_rtol': 1e-10,
'snes_view': None,
'ksp_converged_reason': None,
#'snes_type': 'newtontr', # Trust-region method
'snes_linesearch_type': 'bt', # Critical point line search
}
```

```
mg_params = {
```

}

```
'ksp_type': 'fgmres',
'pc_type': 'mg',
#'pc_mg_type': 'full',
'mg_coarse_pc_type': 'lu',
'mg_coarse_pc_factor_mat_solver_type': 'mumps',
'ksp_gmres_restart': 100,
'ksp_max_it': 500,
```

```
lu_params = {
    'pc_type': 'lu',
    'ksp_type': 'preonly',
    'pc_factor_mat_solver_type': 'mumps',
}
```

```
use_multigrid = True
```

if use_multigrid:

params = params | mg_params

else:

```
params = params | lu_params
```

F_diffusion = inner(F_diffusion, as_vector([1, 1]))*dx

scheme = time_stepping_scheme(U, test_U, [F_diffusion, F_phase], [], time_coefficients = as_vector([1,1,1,1,1]),

bcs = bcs,

```
params = params)
```

```
p_n = inner(as_vector([-1,3,1,0]), ps)
```

```
expressions = {'c': c, 'ps': ps, 'P': as_vector([P[0], P[1], P[3]]), 'mu': mu,
    'p_n': p_n}
writer = writer(['c_mesh', 'phase'], expressions, mesh, "output/parameters_test
    /T=1500C_nuc/output.pvd")
```

```
t_nuc = []
nuc_centres = []
nuc_phases = []
```

solve_time_series(scheme, writer,

```
t_range = [0, .1, 1e7],
iter_t_max = 1e6,
max_dt_change = 1.2,
```

```
eps_t_target = .1,
eps_s_target = .2,
nucleate = False,
centres = nuc_centres,
rad = interface_width*4,
x=x,
interface_width = interface_width,
FuncU=U.sub(1),
t_nuc = t_nuc,
nuc_phase = nuc_phases,
write_freq = 1000
)
```

B.2. THERMODYNAMIC POTENTIALS FILE

```
from thermo_potentials.systems import equil_partition, quadratic
from thermo_potentials.systems.collections import collect_sympy_phases
from thermo_potentials.phases.sympy_components import
    build_ideal_solution_elastic, build_interface_phase
import numpy as np
```

```
def build_potential():
```

T = 1273 #Kelvin RT = 8.314*T #mol fraction of sic gas at 1500C/1773K at different ratios # x_SiC_gas = 3.8288e-02 #1MTS:1H2:1Ar #mol fraction of sic gas at 1400C/1673K at different ratios # x_SiC_gas = 3.8288e-02 #1MTS:1H2:1Ar #mol fraction of sic gas at 1000C/1273K at different ratios $x_SiC_gas = 5.4499e-02$ #1MTS:1H2:1Ar #mol fraction of sic gas at 1200C/1473K at different ratios # $x_SiC_gas = 4.1749e-02$ #1MTS:1H2:1Ar

mu0_SiC_solid = -161028 #T=1400c # mu0_Ar = -290457 #T=1400C mu0_SiC_solid = -127610 #T=1000C mu0_Ar = -215263 #T=100C mu0_SiC_gas = mu0_SiC_solid -RT*np.log(x_SiC_gas) print(mu0_SiC_gas)

rho_SiC = 3.09 / 40.11 * 1e6 # 3.21 g/cm^3 / 40.11 g/mol = .08 mol / cm^3

$$kappa_SiC = 186e9*1e-5$$

- rho_Ar = 101e3 / RT # n/V = P / RT = 101 kPa / (8.314 J/(mol K) * 1600 K) = 7.5 mol / m^3
- a_a = build_ideal_solution_elastic([mu0_SiC_solid], T=T, vi = 1/rho_SiC, kappa = kappa_SiC, phase_id = 'a')
- a_b = build_ideal_solution_elastic([mu0_SiC_solid], T=T, vi = 1/rho_SiC, kappa = kappa_SiC, phase_id = 'b')
- a_c = build_ideal_solution_elastic([mu0_SiC_solid], T=T, vi = 1/rho_SiC, kappa = kappa_SiC, phase_id = 'c')
- a_d = build_ideal_solution_elastic([-mu0_SiC_gas,mu0_Ar],T=T, vi = 1/rho_Ar
 , kappa = 1e5, phase_id='d')

a_full = collect_sympy_phases([a_a, a_b, a_c, a_d], rename=False)

y0 = [1, 1, 1, 1, rho_SiC, rho_SiC, rho_SiC , rho_Ar*x_SiC_gas, rho_Ar*(1x_SiC_gas)]

a_quad = quadratic.quadratic_collection(a_full, ['c0', 'c1', 'V_a', 'V_b', ' V_c', 'V_d'], y0 = y0)
print(a_quad)

return a_quad

B.3. TOOLS FILE

from firedrake import *
from firedrake.petsc import PETSc
from numpy import random, ndarray
from firedrake.__future__ import interpolate
import numpy as np
from mpi4py import MPI as pyMPI
import mpi4py

```
def print (* args , ** kwargs) :
```

#Overloads print to be the petsc routine which relegates to the head mpi rank

PETSc.Sys.Print(*args,flush=True)

class writer:

def __init__(self, names, expr_dict, mesh, filename = "output/output.pvd"):
 #Names of native fields and user-defined must be treated differently.

self.names = names #Names of calculated fields
self.mesh = mesh
self.expr_dict = expr_dict

self.file = VTKFile(filename)

self._check_and_reduce_dimensions()

self.functions = {name: Function(self._similar_function_space(expr, mesh), name=name)

for name, expr in expr_dict.items() }

self._check_and_reduce_dimensions()

def _similar_function_space(self, field, mesh):

fd = len(field.ufl_shape)

if fd == 0:

return FunctionSpace (mesh, "CG", 1)

elif fd == 1:

return VectorFunctionSpace(mesh, "CG", 1, dim=field.ufl_shape[0])
elif fd == 2:

return TensorFunctionSpace(mesh, "CG", 1, symmetry=True)

else:

raise ValueError(f"Unsupported_field_dimension:_{fd}")

def _check_and_reduce_dimensions(self):

for name, expr in self.expr_dict.items():

if len(expr.ufl_shape) == 1 and expr.ufl_shape[0] > 3:

print(f'Warning:_Vector_field_"{name}"_has_more_than_3_

dimensions._Truncating_to_3_dimensions.')

self.expr_dict[name] = as_vector([expr[0], expr[1], expr[2]])

def truncate_vector_fields(self, flds):

" " "

Given a list of Firedrake Function objects, returns a new list where any function with a vector dimension > 3 is replaced by a new function that only uses the first three components.

truncated = []

for f in flds:

```
# Check if function has a vector shape and length greater than 3.
```

if hasattr(f, "ufl_shape") and len(f.ufl_shape) == 1 and f. ufl_shape[0] > 3:

print (f'Warning: Function " $\{f.name()\}$ " has dimension $\{f.name()\}$

ufl_shape[0]}._Truncating_to_3_components.')

Create an expression using only the first three components.

truncated_expr = $as_vector([f[0], f[1], f[2]])$

Create a new function space with dimension 3.

V_new = VectorFunctionSpace(f.function_space().mesh(), f.

function_space().ufl_element().family(),

f.function_space().ufl_element().

degree(), dim=3)

 $f_trunc = Function(V_new, name=f.name())$

f_trunc.interpolate(truncated_expr)

truncated.append(f_trunc)

else:

truncated.append(f)

return truncated

```
def write(self, U, time):
```

```
def get_functions(U, names): # Returns tuple of function with correct
    names
```

```
sol = U.subfunctions
for i in range(len(sol)):
    sol[i].rename(names[i],names[i])
return sol
```

```
#print('Writing solution')
flds = list(get_functions(U, self.names))
```

flds = self.truncate_vector_fields(flds)

```
# Update expressions
```

```
f = [self.functions[name].interpolate(expr) for name, expr in self.
    expr_dict.items()]
```

flds = flds + f

self.file.write(*flds, time=time)

def solve_time_series(scheme, writer,

x = None,

interface_width = None,

```
FuncU = None,
        nucleate = False,
        centres = [],
        t_nuc = [],
        nuc_phase = [] ,
        rad = 1,
        t_range = [0, 5e-2, 1e4],
        eps_t_target = .1,
        eps_t_limit = None,
        eps_s_target = 1000,
        eps_s_limit = 1000,
        exit_on_error = False,
        iter_t_max = 1000,
        max_dt_change = 2,
        threshold = 5.14e-2, # 5.14e-2phi value theshold for nucleation
            centre,
        lower_bounds = [0, 0, 0],
        upper_bounds = [10, 10, 5],
        max_nuc_trials = 10,
        write_freq = 1,
        mesh = None,
        #out_file = None
        ):
t, dt, t_end = t_range
iter_t = 0
# if not eps_t_limit:
```

eps_t_limit = 2*eps_t_target

```
if not eps_s_limit:
       eps_s_limit = 2*eps_s_target
   writer.write(scheme.U, 0.0)
   while t<t_end and iter_t<iter_t_max:</pre>
       iter_t +=1
       proceed = False
       print('\n{:n}:_Solving_for_time:_{:6.4g}'.format(iter_t, t+dt))
       try:
           so, eps_t, eps_s = scheme.step(dt)
           print('Converged_with_dt:_{:4.2g}._Estimated_error:_{:4.2g},_max_
              change_{:4.2g}'.format(dt, eps_t, eps_s))
           proceed = True
       except KeyboardInterrupt:
           print ('KeyboardInterrupt_exception_is_caught')
           break
       except Exception as ex:
           print('Failed_with_dt:_{:}{:6.4g}_, n'.format(dt), ex)
           if exit_on_error:
               raise
**********************
#Nucleation block
       if len(centres) == 0:
```

```
nucleate = False
if nucleate == True:
    if t_nuc[0] == 0:
        t_nuc = t_nuc[1:]
    #if t => t_nuc[0]:
    if iter_t == t_nuc[0]:
```

```
#dt = 2e-3
# dt = 1e-3 #force dt value at nucleation time-step
centre = centres[0]
#print("rank = ",COMM_WORD.rank)
#consolidate phi across all parallel processes
try:
    philoc = FuncU.at(centre[0])
except RuntimeError:
    philoc = np.inf*np.ones(FuncU.ufl_shape)
comm = mpi4py_comm(FuncU.function_space().mesh().mpi_comm())
phiglob = np.zeros_like(philoc)
comm.Allreduce(philoc, phiglob, op=pyMPI.MIN)
#check if nucleation site has phi<threshold to avoid nucleating
    over naother phase and interpolating phi value >1
```

```
counter = 0
```

while True:

```
if phiglob.max() > threshold:
    centres = centres[1:]
    centre = centres[0]
    counter +=1
```

else :

break
#exit loop after max_nuc_trials failed loops
if counter > max_nuc_trials or len(centres) == 1:

break

nucleus = create_bubble(centre,rad,x,interface_width) a, b, c=0, 0, 0if nuc_phase[0] == 'a': a = nucleuselif nuc_phase[0] == 'b': b = nucleuselse: c = nucleus $p0 = max_values([a,FuncU[0]])$ $p1 = max_values([b,FuncU[1]])$ $p2 = max_values([c,FuncU[2]])$ $p_{init} = as_{vector}([p0, p1, p2])$ FuncU.interpolate(p_init) centres = centres [1:] nuc_phase = nuc_phase[1:] if len(t_nuc)>1: $t_nuc = t_nuc[1:]$

if iter_t == 1:

scheme.solver.parameters.pop('snes_view',None) # Unset the
snes_viewer so as not to repeat it.

if proceed:

```
if eps_t_limit is not None:
    if eps_t>eps_t_limit:
        print('Time_error_limit_exceeded')
        proceed = False
```

print('Max_solution_change_limit_exceeded')

#proceed = False

if proceed:

Time step is successful and acceptable
t += dt
scheme.accept_step()
dt *= min(
 eps_t_target/(eps_t+le-10),
 eps_s_target/(eps_s+le-10),
 max_dt_change)

else:

```
dt *=.5
scheme.reset_step()
```

Adapt the time step to some metric
#dphase = errornorm(phase,phase_old,'l10')
#print('max phase change', dphase)
#dphase_target = .1

```
#dt.assign(float(dt)*min( (dphase_target/(dphase)), 20)) # Change
    timestep to aim for tolerance
```

if iter_t % write_freq ==0:

writer.write(scheme.U, time=float(t))

```
def concatenate_vectors(vecs):
```

```
# Make this an | operator?
```

return as_vector([item for sublist in vecs for item in sublist])

class time_stepping_scheme:

Defines an object to contain the time stepping

```
def __init__(self, U, test_U, F_td, F_qs, time_coefficients, bcs=[], dt =
```

```
1, nullspace=None, bounds = None, params=[]):
```

```
V = U.function_space()
self.U = U
self.U_old = U.copy(deepcopy=True)
self.dUdt = Function(V)
self.dUdt_old = Function(V)
self.dU = TrialFunction(V)
```

self.bounds = bounds
self.dt = Constant(dt)

problem_steady_state, solver_parameters=params, nullspace=nullspace)

F_time_dependant = inner(elem_mult(time_coefficients,(self.U-self.U_old

)), test_U) * dx - self.dt * $sum(F_td) + sum(F_qs) # F_steady_state$

import numpy as np

r1 = assemble(F_time_dependant)

v = r1.dat.data

print("The_norms_are:", [np.linalg.norm(d, axis=0) for d in v])

```
# TODO: Use TransferManager to transfer the solution. What does this
mean? Does it help?.
TM = TransferManager()
```

self.solver.set_transfer_manager(TM)

```
def step(self, dt):
    self.dt.assign(dt)
    # Explicit time step for initial guess
    print('using_explicit_step')
    self.U.assign(self.U_old + self.dUdt*dt)
    #self.t.assign(self.t + dt)
    so = self.solver.solve(bounds = self.bounds)
```

self.dUdt.assign((self.U-self.U_old)) #Is this slow compared to itnerpolate or vector manipulation? self.dUdt /= dt eps_t = errornorm(self.dUdt, self.dUdt_old)/2*dt #/dt*dt^2 #Estimate current rate of change of solution #eps_s_max = errornorm(self.U, self.U_old, 'l100') #l100 argument doesn't work. no linf option eps_s = self.dUdt.vector().max()*dt return [so, eps_t, eps_s]

def accept_step(self):

self.dUdt_old.assign(self.dUdt)

self.U_old.assign(self.U)

print('\nIntegrals')

for u in self.U.subfunctions:
 for u2 in u:
 print(assemble(u2*dx))

```
def reset_step(self):
    self.U.assign(self.U_old)
    self.dUdt.assign(self.dUdt_old) # update old dUdt
```

def jump_to_steady_state(self):

so = self.solver_steady_state.solve() #If this errors out, nothing else
will execute
print("Solved!")
Only reach this point if solve was successful
self.dUdt.assign(self.U)

self.dUdt=self.U_old deltaU = self.U_self.U_old self.dUdt/=self.dt(0) #self.dUdt.assign((self.U.vector()-self.U_old.vector())/self.dt(0)) #Calculate new dUdt eps_t = norm((self.dUdt-self.dUdt_old)/self.dt(0), norm_type='12')/2* self.dt(0)**2 return [so, eps_t, self.deltaU.vector().max()] def plotJac(self): print('Warning_-_not_tested')

```
import scipy.sparse as sp
import matplotlib.pyplot as plt
indptr, indices, data = petsc_mat.getValuesCSR()
scipy_mat = sp.csr_matrix((data, indices, indptr), shape=petsc_mat.
getSize())
plt.spy(scipy_mat)
plt.savefig('Jacobian.png')
#plt.show()
```

```
def create_bubble(centre, r, x, interface_width):
    def create_bbl(centre, radius, x, interface_width):
        #creates single bubble
        centre = as_vector(centre)
        r = sqrt(inner(x-centre, x-centre))
        return .5*(1.-tanh((r-radius)/(2.*interface_width)))
```

if type(centre) is list or type(centre) is ndarray:

#TODO: If radii is list of same length, zip and make multiples
p_bubbles = [create_bbl(c, r, x, interface_width) for c in centre]
return max_values(p_bubbles)

```
else :
```

return create_bbl(centre, r, x, interface_width)

```
def max_values(lst):
```

```
if len(lst)<=1:
```

```
return lst[0]
```

else :

```
return max_value(lst[0], max_values(lst[1:]))
```

def define_centres_arr(lower_edge,upper_edge,step_size,Lx,dims, rand = False,

```
height = 0:
```

```
nrow = int((((upper_edge - lower_edge)/step_size) + 1)**(dims-1))
```

```
arr = np.zeros((nrow,dims))
```

arr[:,dims-1] = height

 $a = [lower_edge] * (dims - 1)$

for i in range(len(arr)):

```
for j in range(dims-1):
```

```
arr[i,j] = a[j]*Lx
if rand == True:
    arr[i,j] = round(random.uniform(lower_edge,upper_edge),1)
```

```
if dims == 3:
    a[1] += step_size
    if a[1] > upper_edge:
        a[1] = 0
        a[0] += step_size
elif dims == 2:
        a[0] += step_size
else:
```

print("Invalid_number_of_dimensions_entered.")

break

return arr

```
def mpi4py_comm(comm) :
```

```
'''Get mpi4py communicator '''
```

try:

```
return comm. tompi4py()
```

except AttributeError:

return comm

B.4. RANDOM NUCLEI GENERATOR

import numpy as np

import random

n = 100 #number of nuclei

```
nuc_phases = []
```

for i in range(n):

#make list of phase choices

phase = np.random.choice(['a', 'b', 'c'],1, replace=False)

nuc_phases.append(phase[0][0])

print(nuc_phases)

```
nuc_centres = []
Lx = 1e-3
Ly = Lx
Lz = Lx
for i in range(n):
  value1 = np.around(np.random.uniform(0, 1),2).tolist()
  value2 = np.around(np.random.uniform(0, 1),2).tolist()
  value3 = np.around(np.random.uniform(0, 1),2).tolist()
```

nuc_centres.append([[value1*Lx,value2*Ly,value3*Lz]])
print(nuc_centres)