Multi-Scale Study of Spark Plasma Sintering for Processing of Graphene-SiC Ceramic Composites

Nicholas Wang, Edward Lin, Steven Kotowski, Harmanpreet Singh, Christopher Conner, Alec Roskowinski

THE DEPARTMENT of MATERIALS SCIENCE AND ENGINEERING

Capstone Project Overview

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  - Results
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  - Methods
  - Results
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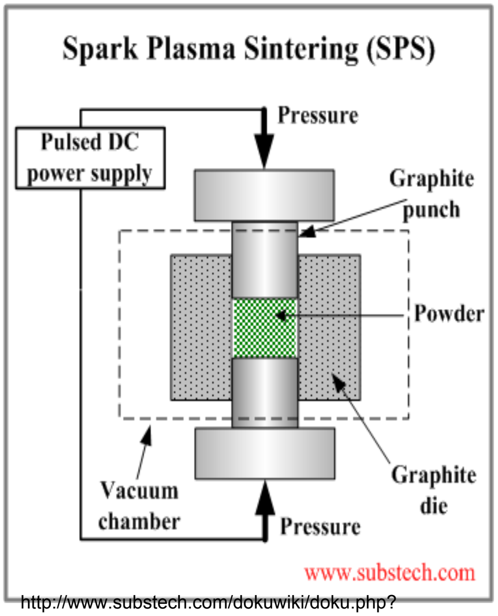
Background & Motivation

- Recent studies show potential to fabricate graphene-SiC composites through spark plasma sintering (SPS), however mechanisms of graphene formation and SPS were not explained
- SPS is a powder consolidation method in which densification is achieved by application of electric current and uniaxially applied pressure in a rigid die
- SPS simulations for SiC powder have not been attempted, even though SiC is a widely used ceramic

- Study of SPS for graphene-SiC can give insight on mechanisms of SPS and lead to reliable future fabrication
- Graphene-SiC composites have potential novel applications due to their mechanical and electrical properties



http://www.substech.com/dokuwiki/doku.php?id=spark_plasma_sintering

MSE Aspects & Previous Work

MSE Aspects

- Study the effect of processing parameters on material properties (final density, mechanical properties, chemical composition)
- Kinetics, thermodynamics, macroprocessing, chemistry, differential equations, and mechanics

Previous Work

- Terrones and Miranzo et al. showed that graphene-SiC can be fabricated through SPS, only focused on electrical properties and applications
- Most of the modeling work on SPS has been limited to the numerical analyses of temperature and electric current distributions during SPS, neglecting sintering/densification
- Olevsky et al. proposed method of a combined meso/macro-scale analysis of sintering kinetics for SPS of Alumina
- McWilliams et. al. also follows a similar approach for Tungsten

Design Goals

- Determine conditions necessary for graphene formation
- Accurately simulate SPS processing conditions using COMSOL
- Fabricate a graphene-SiC composite sample to validate simulation results

Technical Approach: Modelling

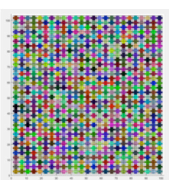
Graphene Formation Model

- Epitaxial graphene forms through thermal desorption of Si atoms from SiC surfaces, remaining C atoms form graphene given appropriate conditions
- Analytical model of SiC constituent vapor pressures vs. temperature

Micro/Meso-scale Grain Evolution Model

- Following Olevsky et al., grain growth simulation of discrete particles using Kinetic Monte Carlo (KMC) & Metropolis algorithm in Matlab
- Determination of constitutive sintering parameters to be used in macro-scale model

Initial Microstructure



- 850 hexagonal grains
- 33% porosity
- uniform distribution

KMC

eg. new state of grain(qi) depends on neighbor states (qj)

3	3	2
3	1	2
3	4	2

P(2)=3/8
P(3)=1/2
P(4)=1/8

Metropolis

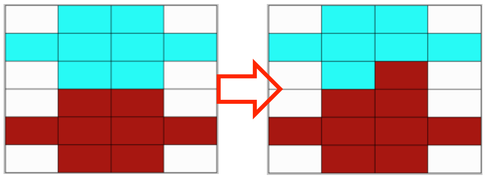
eg. accept/reject new state based on:

$$E = \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{8} \begin{cases} \left(1-\delta(q_i,q_j)\right) for\ grain \\ \left(3-3\delta(q_i,q_j)\right) for\ pore \end{cases}$$

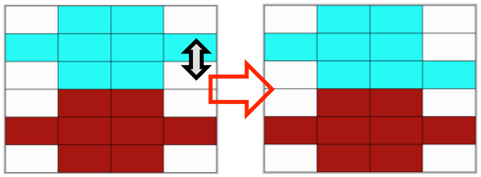
$$P = \begin{cases} \exp\left(\frac{-\Delta E}{k_B T}\right) & \text{for } \Delta E > 0 \\ 1 & \text{for } \Delta E \leq 0 \end{cases}$$

Technical Approach: Modelling (cont.)

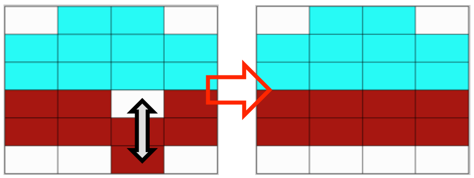
Grain Growth



Pore Migration



Vacancy Annihilation



Macro-scale SPS Model

- Simulates SPS mechanisms (electric currents, heat transfer, applied pressure & densification) using COMSOL Multiphysics 4.1 FEM with appropriate initial values and boundary conditions

Electric Currents

Steady state charge cons:

$$\nabla \cdot \vec{J} = 0$$
$$\vec{J} = \sigma \vec{E}$$
$$\vec{E} = -\nabla V$$

Heat Transfer

Energy cons. and heat radiation:

$$\rho C_p \frac{dT}{dt} = \nabla \cdot (k \nabla T) + Q$$
$$Q = \vec{J} \cdot \vec{E}$$

$$-\boldsymbol{n} \cdot (-k \nabla T) = \epsilon \varepsilon (T_{amb}^4 - T^4)$$

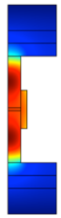
Continuum Sintering Eq.

$$\sigma_{ij} = \frac{\sigma(W)}{W}\left[\varphi \dot{\varepsilon}_{ij} + \left(\psi - \frac{1}{3}\varphi\right)\dot{e}\xi_{ij}\right] + P_L \xi_{ij}$$

$$\sigma(W) = \bar{A} T^m \exp\left(\frac{m \Delta H}{RT}\right) W^m$$
$$W = \frac{1}{\sqrt{1-P}} \sqrt{\varphi \dot{\gamma}^2 + \psi \dot{e}^2}$$

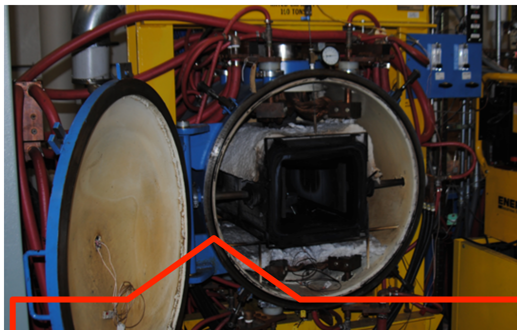
$$\frac{\dot{P}}{1-P} = \dot{e}$$

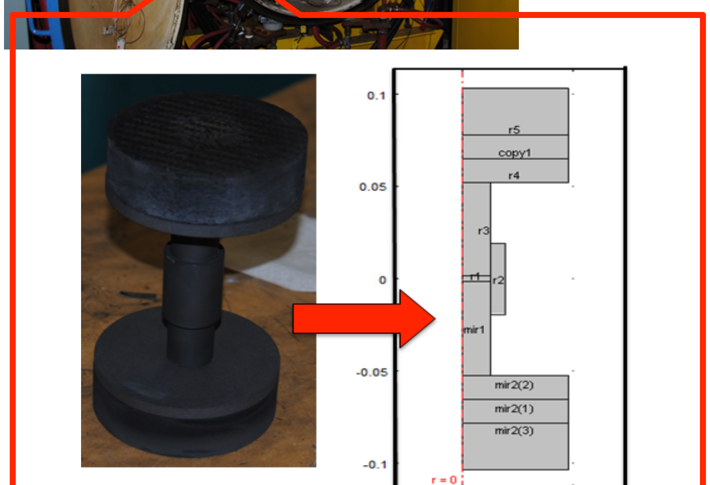
2-D Axisymmetric geometry



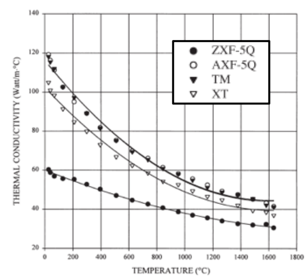
Technical Approach: Modelling (cont.)

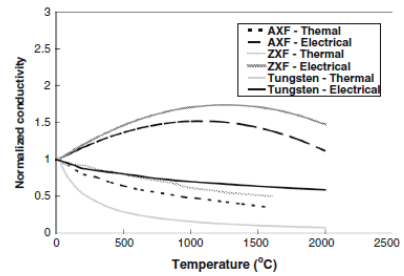
SPS machine at ARL:





Graphite Properties (Taylor&Groot, McWilliams et al.)



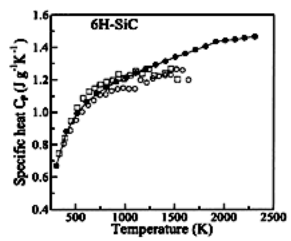


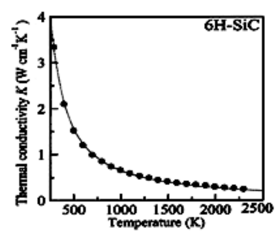
Property	Value @ 20 °C

σ = 5.38e4 S/m

k = 60 W/(m K)

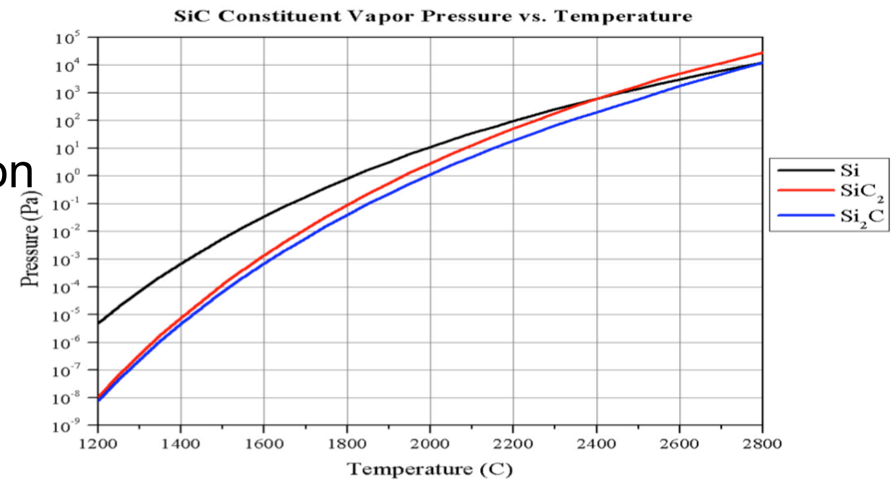
SiC Powder Properties (Nilsson et al., Miranzo et al.)





σ = (1-P)8.3e-5 S/m

Results: Modelling

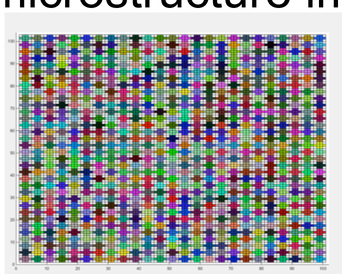


Graphene Growth by Silicon Sublimation

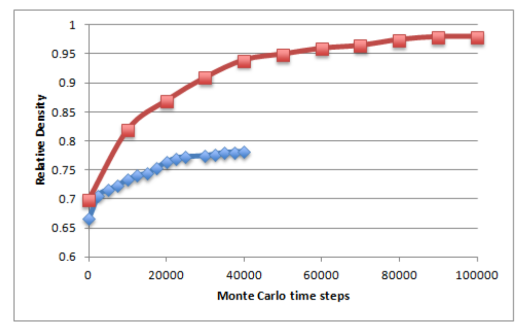
- Experimental data from Lilov, S.K.
- Vacuum/inert gas required to avoid reaction of C atoms with H_2 or O_2
- Graphene formation possible from 1200C-2200C depending on vacuum

Micro/Meso-scale Grain Evolution

- Simulation ran for 40,000 timesteps
- ImageJ used to analyze microstructure images
- Deviation due to difference in vacancy annihilation frequency, but trend is still similar


Microstructure Simulation: 0 MC steps


Microstructure Simulation: 40,0000 MC steps

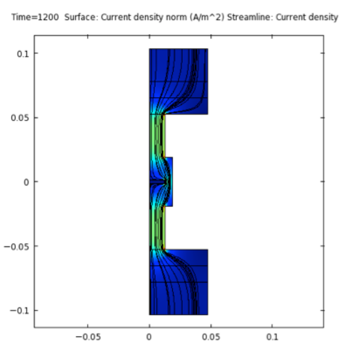


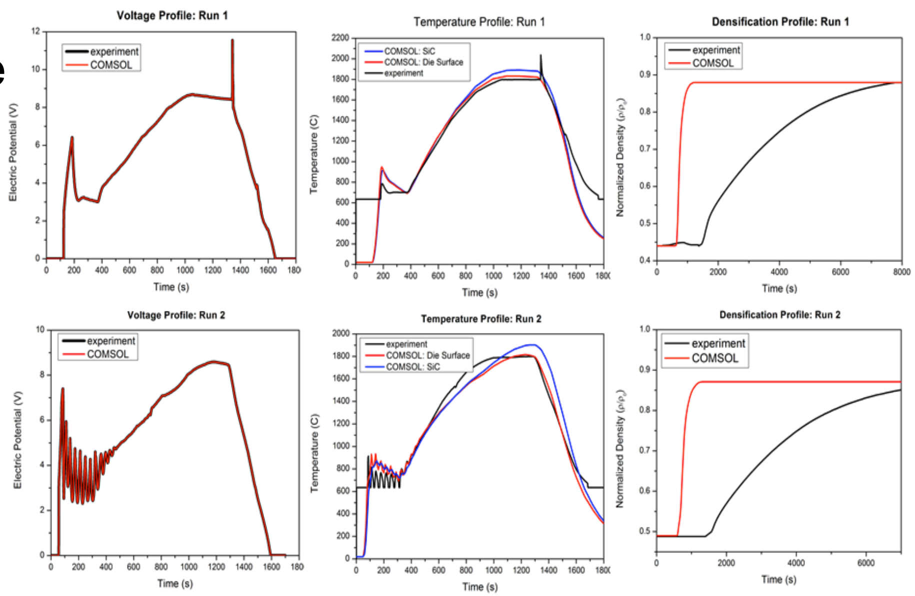
Results: Modelling (cont.)

Macro-scale SPS Model

- Densification derived from sintering equations, solved in Comsol: $\dot{P} = (1-P)\left[\left(\frac{P_L - \bar{\sigma}}{AT^m \exp\left(\frac{m\Delta H}{RT}\right)}\right)\frac{\sqrt[m-1]{1-P}}{\sqrt[m+1]{\frac{2}{3}\varphi+\psi}}\right]^{1/m}$

- No current flow through sample
- Temperature predictions fairly accurate
- Densification deviations can be attributed to non-ideal experimental conditions and assumptions made in COMSOL





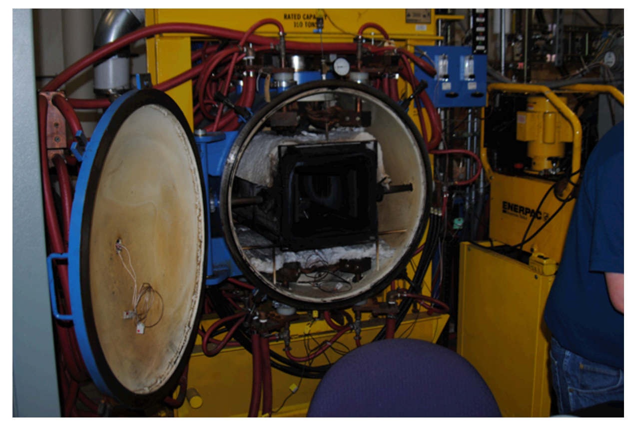
Technical Approach: Prototype

Powder Mixing

- Powder composition: α-phase Silicon Carbide, α-phase Al_2O_3 (2 wt%), α-phase Y_2O_3 (5 wt%) suspended in 150 mL ethanol per batch
- Steps: 1) Attrition milled for 27 hours 2) Heated overnight at 100℃ 3) Ground with mortar and pestle

SPS Fabrication

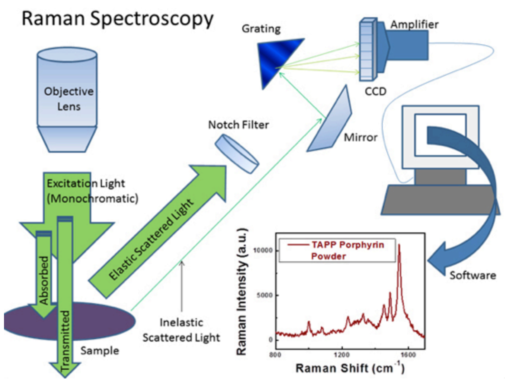
- Each sample contained 4 grams of powder in a 1in diameter graphite die
- Sintered in a 4 Pa vacuum with less than 100psi uniaxial loading due to machine constraints
- Temperature profile taken from Terrones' patent, with additional 700℃ soak at start



Technical Approach: Prototype (cont.)

Characterization

- Formation of graphene determined by Raman Spec.
- Changes in energy (Raman shift) of monochromatic light hitting the sample gives information on bonding
- Relatively simple technique commonly used for graphene study

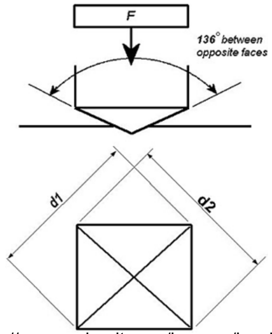


http://www3.nd.edu/~kamatlab/images/Facilities/raman%20spectroscopy.jpg

Mechanical Testing

- SiC is an extremely hard material, many indenters cannot scale this high
  - Vickers hardness test required
    - 30kgF, 10 s hold
    - indent diagonals measured, and HV calculated

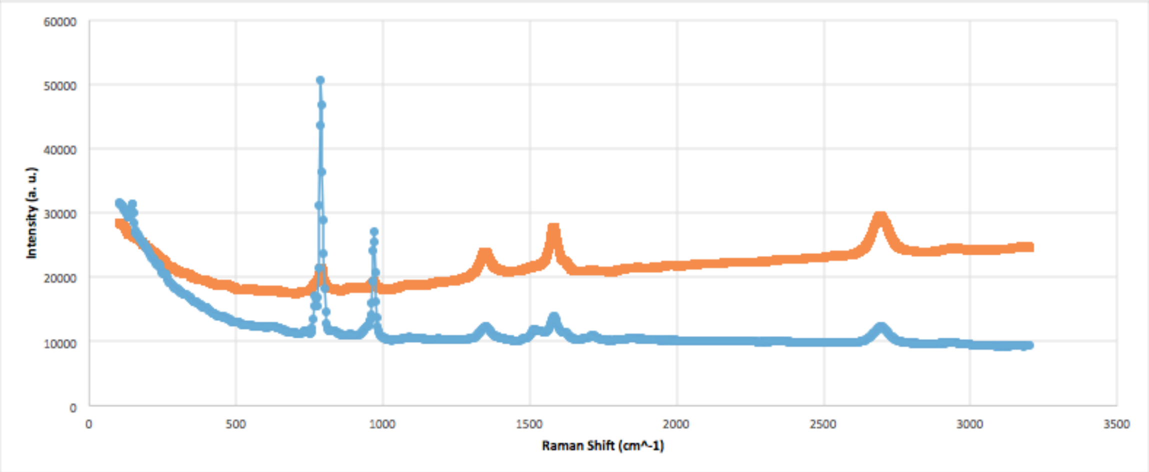
$$HV = \frac{F}{A} \approx \frac{1.8544F}{d^2}$$



http://www.aeisndt.com/images/hardness-testing2.jpg

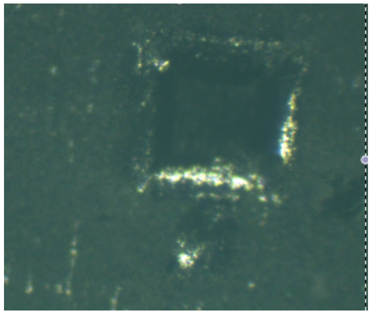
Results: Prototype

Characterization



- Raman results confirmed graphene presence in our samples
- Hardness values not as high as patent samples
  - available processing did not yield fully dense samples
  - longer sintering time resulted in poor hardness
- Future testing may include Raman mapping, SEM imaging, and additional mechanical testing on fully dense samples

Mechanical Testing



Hardness (HV)	
Sample 4	Sample 7
1760	820.7
1436	598.8
1347	820.7

Ethics & Environmental Impact

- Computer modeling of sintering process has no real ethical or environmental impact
- All chemicals used in the process have minimal environmental impact so long as handled properly and should be easily disposed of
- No ethical concern, little risk with great potential benefit in electrical and structural applications
- Environmental impact may increase as production increases but is not yet possible to produce at high volumes

Intellectual Merit & Impact

Intellectual Merit

- Provide insight regarding mechanisms of graphene formation on SiC
- Propose a method of future modelling for SPS of SiC powder (and other materials)
  - Future research requires determination of several material parameters for more accurate results

Impact

- Provides foundation for an understanding of the mechanisms of electric current assisted sintering of SiC
  - Time, materials, and money can all be saved through better processing design
  - Optimization can result in more reliable processing of SiC-graphene composites for potential electrical and structural applications
- Spark more research into modelling of SPS

Conclusions & Future Work

- Potential for epitaxial graphene to form between 1200C-2200C depending on vacuum pressure
- SPS model accurately simulated joule-heating, densification predictions showed deviations from experimental results
- Confirmed presence of graphene in prototype, mechanical testing inconclusive

Looking Forward…

- MD simulation of Si sublimation and graphene formation
- Grain growth algorithm for different initial microstructures/more time steps
- SPS fabrication with applied pressure to compare with simulation results
- Intensive mechanical testing to determine potential for high hardness/toughness applications (body armor)
- SPS optimization in COMSOL

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  - Dr. Aldo Ponce and Dr. Robert Bonenberger
  - MEMIL, UMERC, SAC, VCL, DIT

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