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

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Background & Motivation

It was recently shown by Terrones and Miranzo et al. that graphene-SiC composites could be fabricated by densification of SiC powders with in-situ graphene formation through the process of spark plasma sintering (SPS). SPS is a powder consolidation method in which densification is achieved by the simultaneous influence of electric current and mechanical pressure. Currently, predictive models of SPS are limited. The formation of graphene in SiC is also never explained by the original researchers. The objective of this Capstone project is to create a predictive model of graphene formation and SPS in order to better understand the mechanisms of graphene-SiC fabrication.

Intellectual Merit

- Predictive model of SPS for SiC has never been done before, even though SiC is a widely used ceramic
- Modeling of SPS in general is limited, most studies focus on electric current distribution instead of constitutive models of powder consolidation
- Very little research on graphene-SiC for mechanical properties

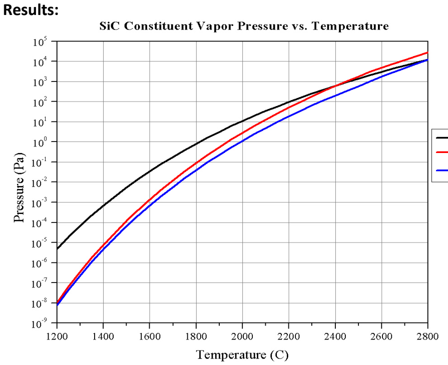
Design Goals

- Determine conditions necessary for graphene formation on SiC
- Accurately simulate SPS processing using COMSOL
- Fabricate a graphene-SiC sample to validate simulations

Graphene Formation Modelling

Epitaxial graphene forms on SiC grains due to thermal desorption of Si atoms from the lattice. To determine conditions for graphene formation, experimental data from Lilov (1995) was analyzed.

Results:



- At conditions below the vapor pressure of Si and above SiC_2 and Si_2C, Si atoms selectively sublimate from SiC lattice and the remaining C atoms form graphene
- From the data, graphene potentially forms between 1200°C-2200°C depending on the vacuum pressure
- Conventional sintering methods of SiC do not meet conditions for graphene formation

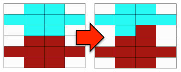
Micro/Meso-Scale Grain Evolution Modelling

A discrete particle model in the form of a Kinetic Monte Carlo and Metropolis algorithm is necessary to accurately simulate grain growth mechanics by determining parameters to be utilized in the macro-scale SPS model.

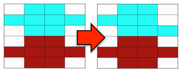
Simulated processes:

$$E = \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{8}\left(1-\delta(q_i, q_j)\right) \qquad P = \begin{cases} \exp\left(\frac{-\Delta E}{k_B T}\right) & \text{for } \Delta E > 0 \\ 1 & \text{for } \Delta E \le 0 \end{cases}$$

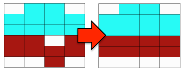
Grain Growth



Pore Migration

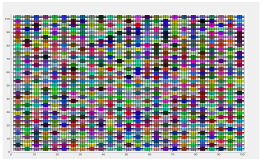


Vacancy Annihilation

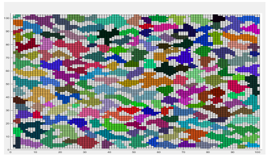


Results:

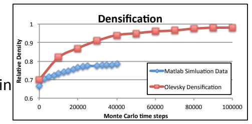
Initial microstructure



After 40,000 timesteps



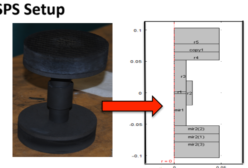
- Deviation from Olevsky data due to difference in vacancy annihilation attempts
- But both data sets resemble same trend in densification



Macro-Scale SPS Modelling

COMSOL Multiphysics 4.1 utilized to simulate SPS due to its ability to couple and simultaneously solve problems involving multiple physical phenomena through FEM. Sintering phenomena considered include electric currents, heat transfer, and densification based on Olevsky's continuum theory of sintering (1998)

SPS Setup



COMSOL equations

Electric Current

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

Heat Transfer

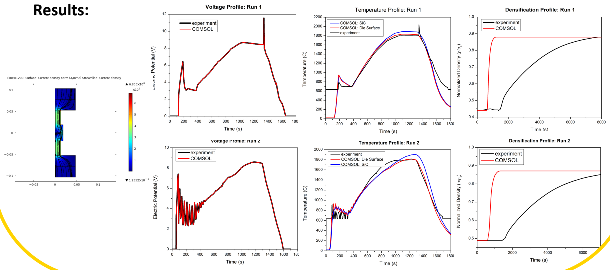
$$\rho C_p \frac{dT}{dt} - \nabla \cdot (k\nabla T) = \sigma |\nabla V|^2$$

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

Densification

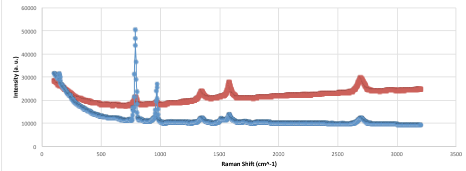
$$\dot{P} = (1-P)\left[\left(\frac{P_L - \bar{\sigma}}{AT^m \exp\left(\frac{m\Delta H}{RT}\right)}\right)\frac{\sqrt[m-1]{1-P}}{\sqrt[m+1]{\frac{2}{3}\varphi + \psi}}\right]^{1/m}$$

Results:

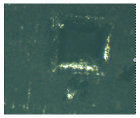


Sample Characterization and Testing

Powder mixing was carried out following the methods of Miranzo et al. (2013) and Terrones and sintered at Army Research Lab using their SPS.



- Raman Spectroscopy confirmed graphene presence throughout our samples
- Peaks around the 1500 cm^{-1} and 2700 cm^{-1} Raman shifts correlate to graphene bonds
- Large peaks at 796.5 cm^{-1} and 973 cm^{-1} correspond to SiC



- Vickers Hardness Testing performed
- Resulting samples' hardness values expected to be similar to SiC (at least 2000 HV)
- SPS could not fully densify samples without adequate applied pressure
- Lack of fully dense samples and long sintering times drastically reduces mechanical properties, although we obtained promising values for future work

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

Conclusions & Future Research

- Epitaxial graphene conditions were determined to be at temperatures of 1200C-2200C under vacuum or inert gas
- SPS simulations were accurate in predicting temperature conditions. Densification predictions deviated from the experiment, due to non-ideal conditions and assumptions made in the simulation
- The presence of graphene was determined by Raman spec, confirming the model results.

Looking forward…

- Grain growth for different microstructures/more time steps
- Apply model to densification under applied pressure
- Intensive mechanical testing to determine potential applications
- Optimize SPS process in COMSOL

Acknowledgements

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