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Spark Plasma Sintering (SPS) Update for the Fuel Conversion Effort at the Transient Reactor Test Facility

Seongtae Kwon, Ben Coryell, Bryan Forsmann, Ricardo Castro, Arseniy Bokov, Eric Eyerman, Erik Luther

May 2017

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Spark Plasma Sintering (SPS) Update for the Fuel Conversion Effort at the Transient Reactor Test Facility

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October, 2017

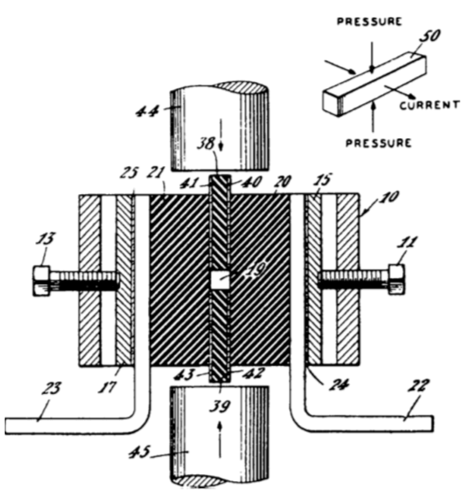


Fig. 23. Schematic representation of the process patented by Balaguer. Adapted from Balaguer [142].

Original US patent in 1906 for spark plasma sintering graphite for fuel.

Team and Collaborators

- Boise State University, CAES
  - Bryan Forsmann
- University of California Davis
  - Ricardo Castro, Arseniy Bokov
- California Nanotechnologies
  - Eric Eyerman
- Idaho National Laboratory
  - Seongtae Kwon
- Los Alamos National Laboratory
  - Erik Luther

Sintering Graphite Cylinders for TREAT with SPS

Significance

The ability to spark plasma sinter graphite demonstrates a significant cost saving technique over relevant processing conditions (e.g., time, temperature, and pressure) as conventional block compaction and sintering.

Latest Update from CalNano

- Cal Nano made a custom WC die for making these samples.
- Traditional graphite dies were too weak for the sintering parameters and part dimensions required. High strength graphite was used for punches.
- WC die dimensions: 2.008” ID x 3” OD x 3” LG
- Final Sintered 2” cylinder 2” tall is partially intact with high density regions (>2 g/cm^3) in place (under development)
- 3 Graphite only and 1 mixed fully sintered 2” diameter by 0.8” tall samples.

SPS 7.40 Mk IV

Die Set

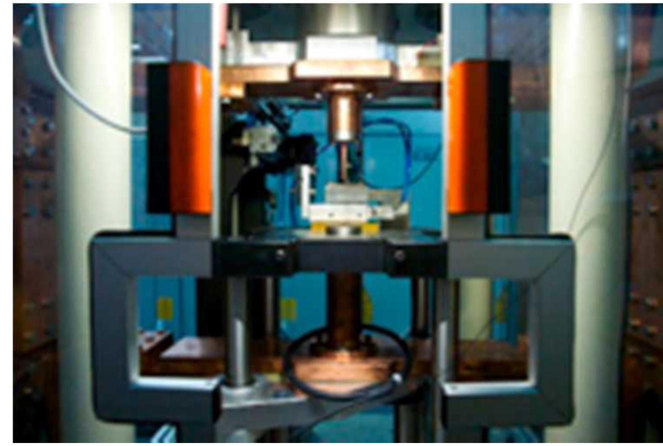
Sintered Pellet

Spark Plasma Assisted Sintering

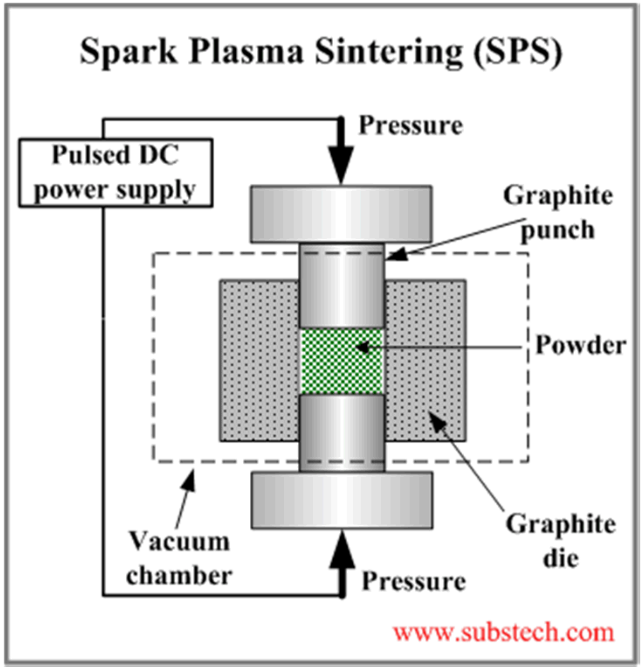
Electrically Assisted Compaction: Spark assisted thermal compaction makes sintering blocks faster and at a lower cost per volume compared to conventional compacted graphite.

Advantages

- Electrical current assisted sintering is a well established technique since 1906 (+pressure year 1913)
- Low to high temperatures can be readily achieved (>2000° C)
- Commercially available to metric tons
- Higher densities achieved than demonstrated with warm pressing
- Only graphite powders are consumed (no resin, hardeners).
- Commercially available to accommodate larger sizes up (4” diameter).
- Significantly lower cost of production.



Differences with Current Pressing Method



Materials Input

- Powder mixture of natural graphite powder flake and oxide
- No organic resins or hardeners

Fabrication

- Operates an uniaxial press configured with electrical bias and heating element under vacuum
- Pressing, sintering, and annealing in one step

Outputs

- Sintered cylinders that can be machined into shapes (Different shapes are possible)
- 10-30 cylinders per day are possible
- Systematic analysis on scale-up to 2” to 4” diameter cylinders is ongoing.

Achievements

- Ongoing efforts in TREAT are showing the density above 2 g/cm^3
- Sintered sizes 10 mm, 20 mm, and 2” (partially) demonstrated

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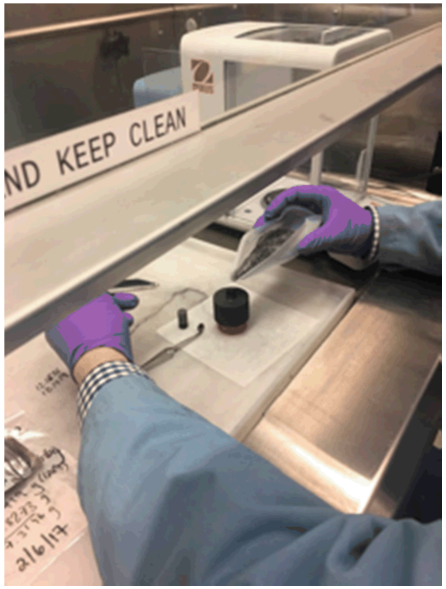
Program Relevant Questions

Progress

- **Can we spark plasma sinter larger samples?**
- **How do processing variables (time, temperature, pressing direction) interact with achieved spatial density?**
- **What is the fraction of cracks determined by imaging? How does it compare with current blocks?**
- **What is the carbon chemistry and resulting structure following spark plasma sintering?**

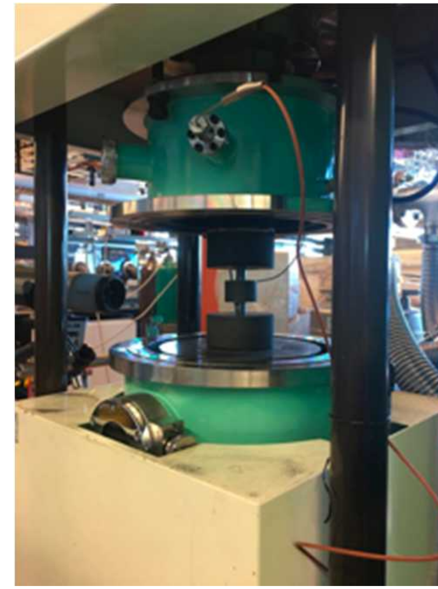
Operation

Loading the charge



Setting up the die

Validate Setup



Evacuate Press

Run the cycle

Heat and apply max load

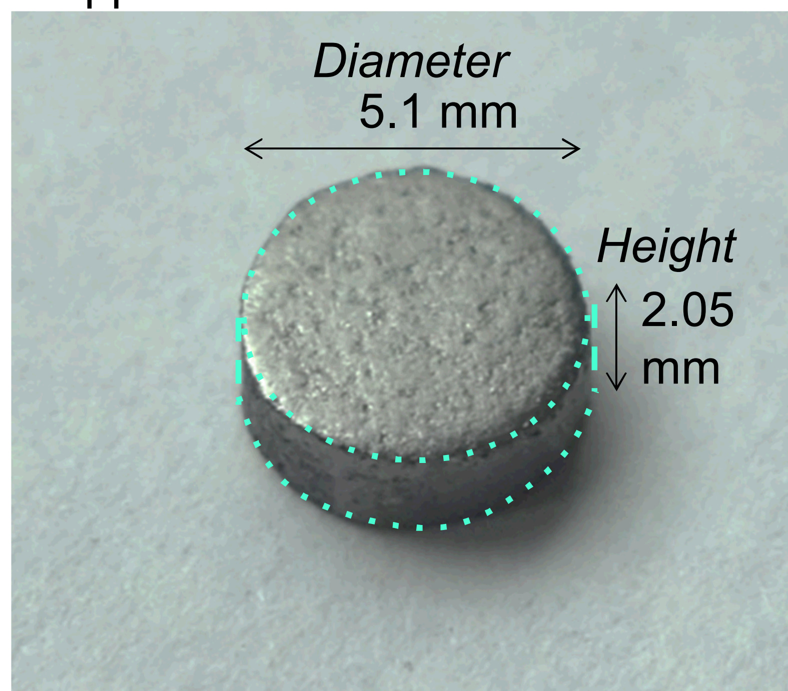
Material Inputs and Outputs

Material Input:

- Asbury Graphite Mills, Grade 3482
- Natural graphite (QA-257969, QA258233)

Sintered Pellet Output:

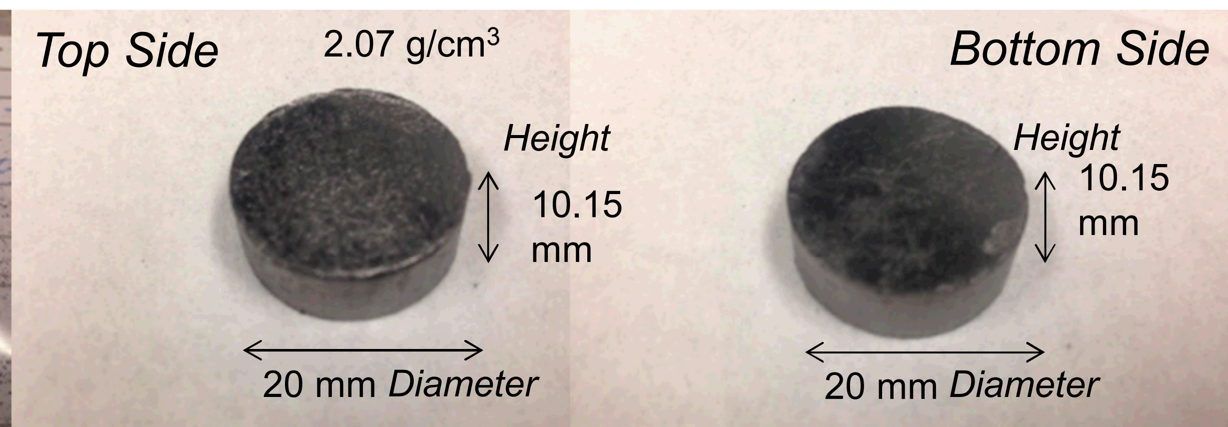
- Sintered 2 pellets (5.1 mm x 2.05 mm)
- 2.04 g/cc (90% theoretical density) and 2.1 g/cc
- Pellet 1: 300 MPa at 700° C, 2.1 g/cc
- Pellet 2: 230 MPa at 800° C, 2.04 g/cc
- Heat cycle: 560° C in 5 minutes, 700° C in 7 min
- Load applied from 8 to 10 minutes



SPS Sintering Conditions Tested at CalNano

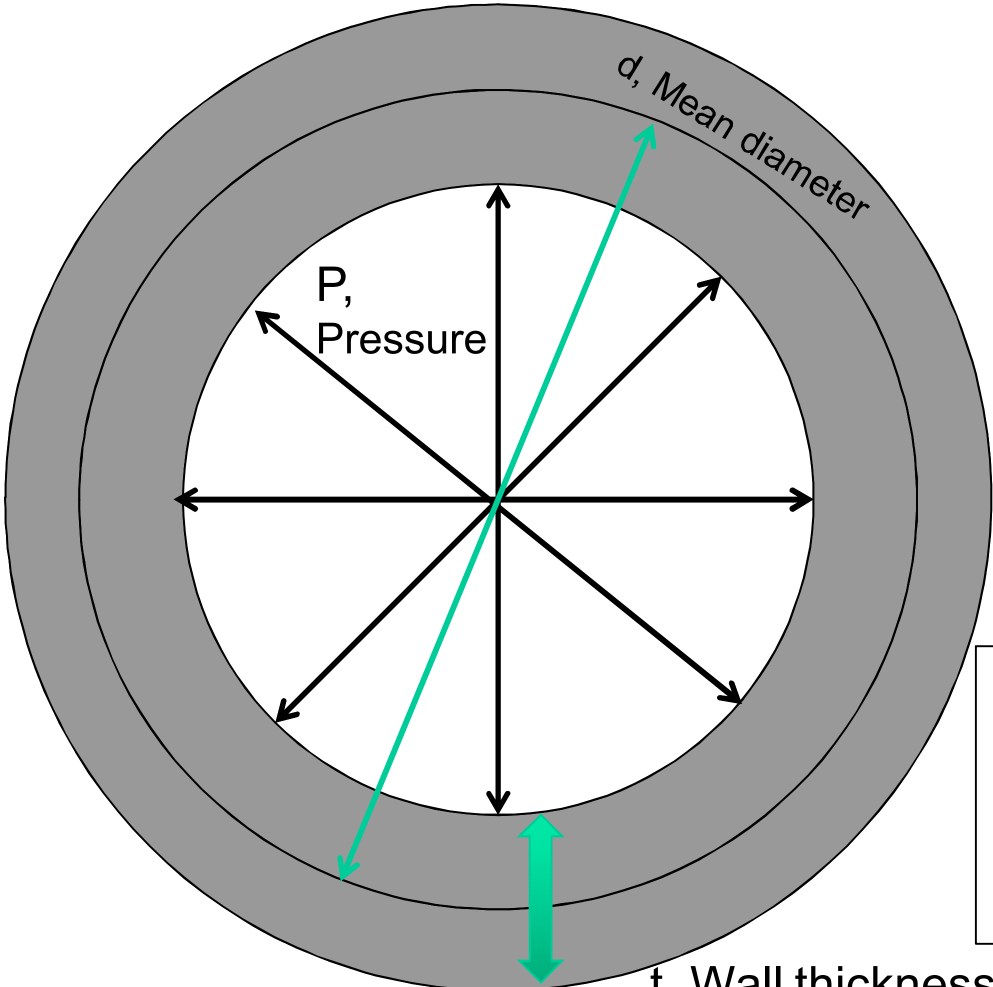
Size (OD)	Temp (C)	Pressure (Mpa)	Hold Time	Die Material	Result
20 mm	900	80	5	Graphite	No consolidation
20 mm	1150	80	5	Graphite	No consolidation
20 mm	1200	95	5	Graphite	2.06 g/cm3
20 mm	1000	95	5	Graphite	2.05 g/cm3
2”	1000	75-95	N/A	Graphite	Broken Tooling
2”	1000	50	10	Graphite	No consolidation
2”	1000	95	5	WC	Low density
2”	1000	95	10	WC	Fully sintered (0.8” tall)

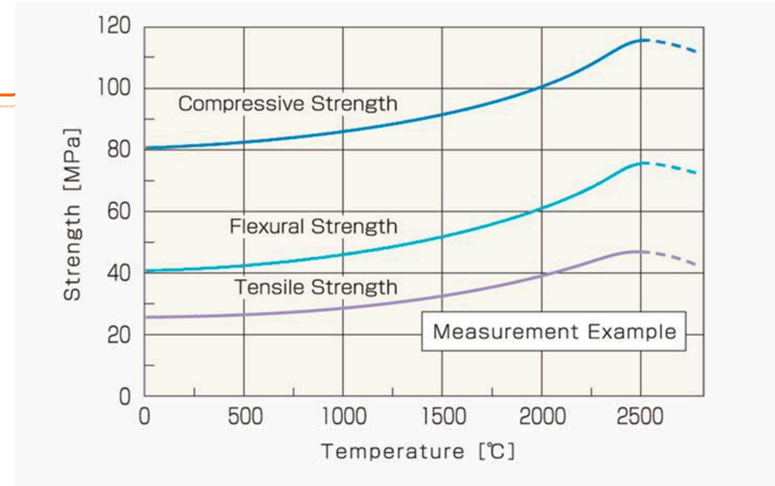
Cold Pressed Graphite Sample



Spark Plasma Sintered Graphite Sample

Challenge Pressing to Larger Sizes and Heights





Equating isostatic wall stress:

$$\sigma_{Long} = \frac{F}{A} = \frac{Pd^2}{(2t+d)^2 - d^2}$$

Approximating isostatic wall stress:

$$\sigma_{Long} \approx \frac{Pd^2}{4t}$$

- Balancing isostatic hoop stresses is a function of the inner and outer diameters as well the mechanical failure points of die material.
- To date a 2” (Inner diameter) tungsten carbide has shown promise with temperatures nearing 1000°C and 100 Mpa of applied pressure

Summary

Initial Assessment: Spark assisted thermal compaction achieves high densities (> 1.85 g/cc) and can accommodate sintering above 100 MPa at temperatures below 1200 ° C. Future sintering studies will require better tooling and commercial setup to demonstrate larger sizes (1”, 2”) at commercial vendors (CalNano Corp). In addition, bimodal graphite particle sizes and different natural graphite blends may accommodate better sintering and densities.

- Cal Nano successfully consolidated INL material at 1000 and 95 Mpa with 2” diameter sizes.
- SPS 7.40 Mk IV unit, can produce the volumes needed for the program.
- If INL needed to purchase a SPS unit of their own, Cal Nano is also the official North American representative for the equipment manufacturer FUJI-SPS. Cal Nano would help with the purchase, installation, training and servicing of a new SPS unit.

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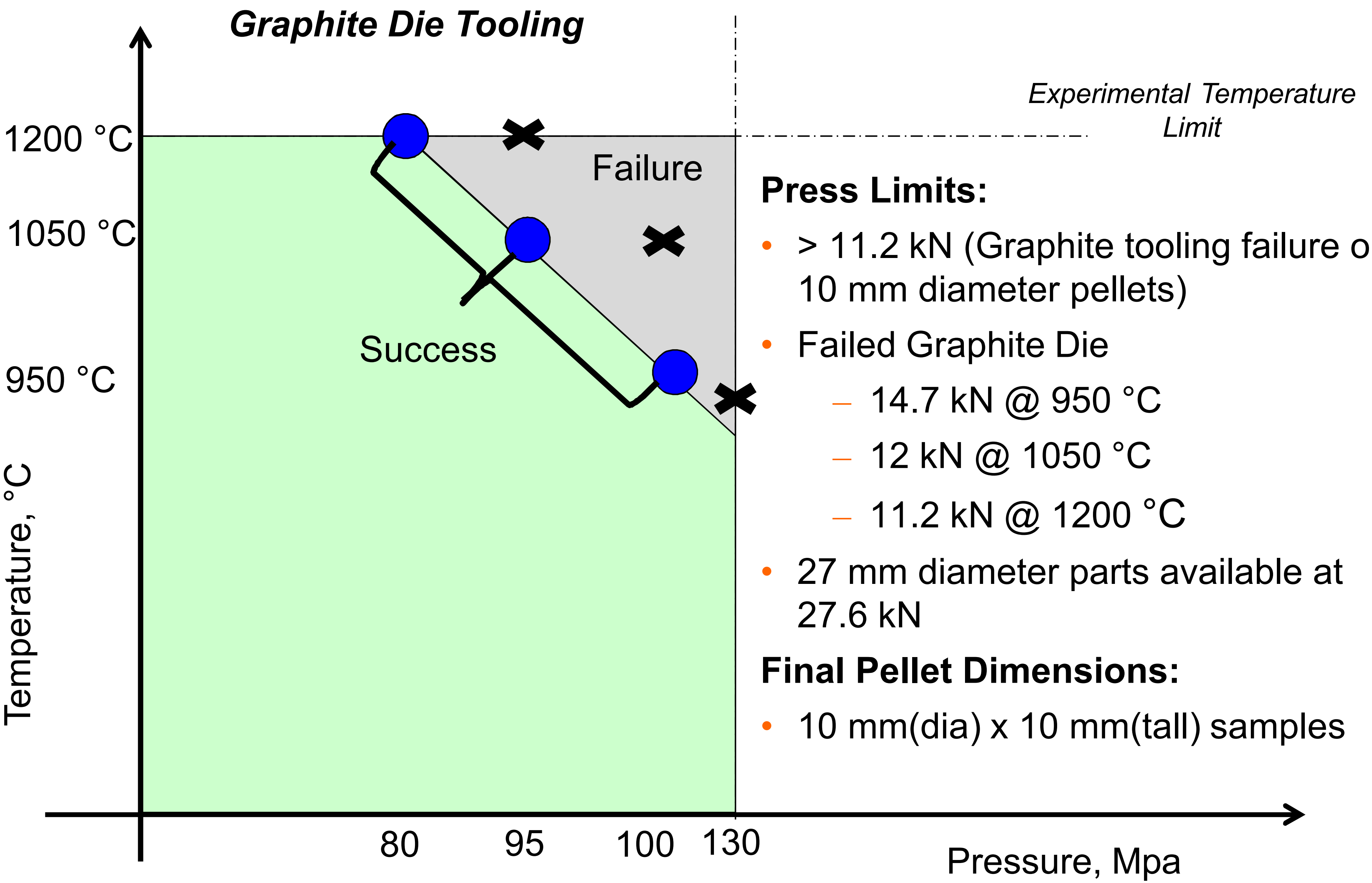
Supplementary Slides follow

Spark Plasma Sintering 10 mm Pellets on Dr.Sinter



Press Limits:

- > 11.2 kN (Graphite tooling failure on 10 mm diameter pellets)
- Failed Graphite Die
  - 14.7 kN @ 950 °C
  - 12 kN @ 1050 °C
  - 11.2 kN @ 1200 °C
- 27 mm diameter parts available at 27.6 kN

Final Pellet Dimensions:

- 10 mm(dia) x 10 mm(tall) samples

Spark Plasma Sintered Samples

Archimedes Density and Porosity Measurement

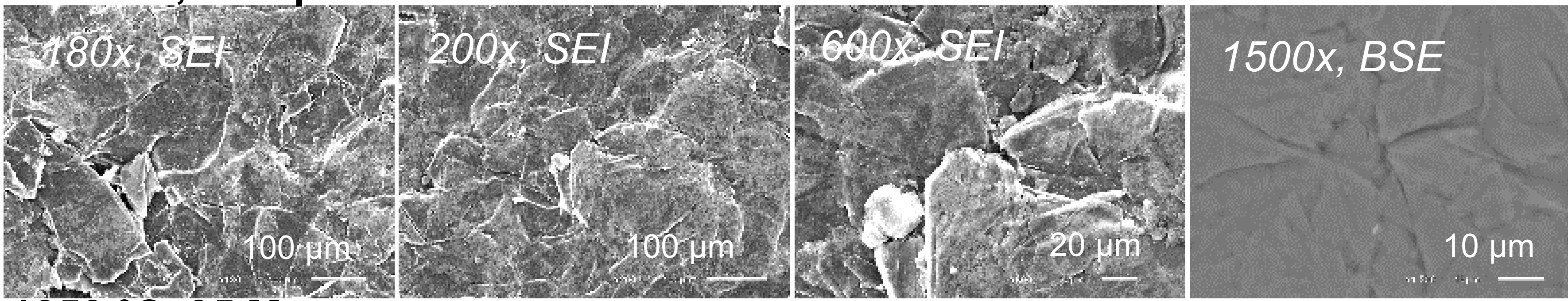
Sample	Dry Weight (g)	Suspended Weight (g)	Saturated Weight (g)	Weight of Water in Pore Space (g)	Pore Volume (cm3)	Porosity (%)	Bulk Volume (cm3)	Density (g/cm3)
950C, 100 Mpa	0.3798	0.1793	0.3821	0.0023	0.0023	1.1341	0.2028	1.8690
	0.3798	0.1791	0.3832	0.0034	0.0034	1.6659	0.2041	1.8571
	0.3796	0.1788	0.3831	0.0035	0.0035	1.7132	0.2043	1.8543
	0.3792	0.1789	0.3842	0.005	0.005	2.4355	0.2053	1.8434
1050 C 95 MPa	0.3662	0.1704	0.3722	0.006	0.006	2.9732	0.2018	1.8110
	0.3661	0.1711	0.3722	0.0061	0.0061	3.0333	0.2011	1.8168
	0.3665	0.1708	0.3724	0.0059	0.0059	2.9266	0.2016	1.8143
1200 C 80 Mpa	0.2835	0.1314	0.2855	0.002	0.002	1.2979	0.1541	1.8360
	0.2834	0.1308	0.2857	0.0023	0.0023	1.4848	0.1549	1.8259

Spark Plasma Assisted Compaction: 10 mm (diameter) x 10 mm (tall) samples were used to investigate the pressing parameters and the effect on the final material outcomes.

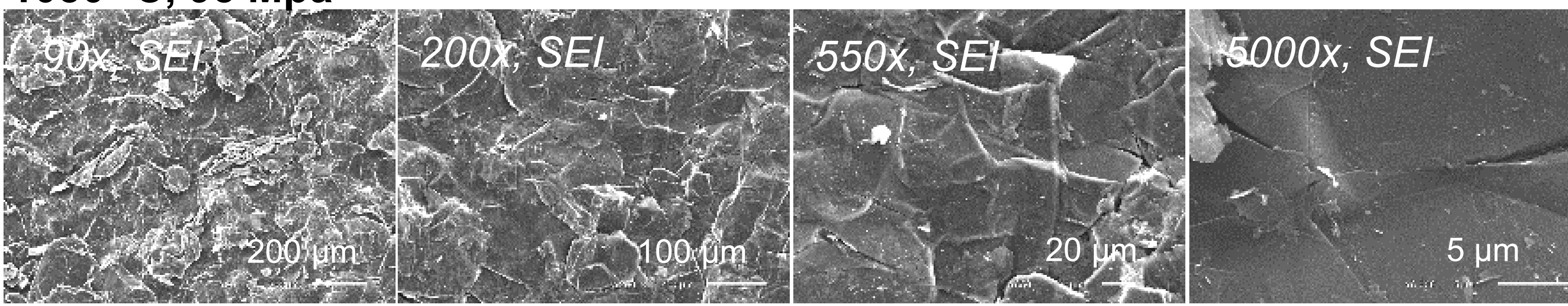
SEM of Fractured Sintered Pellets

- + same electrical bias + high temperature + pressure

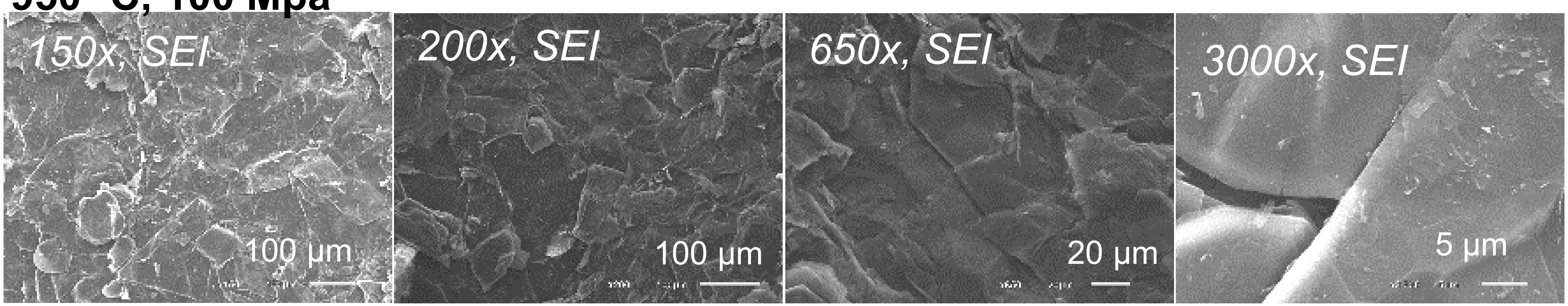
1200 °C, 80 Mpa



1050 °C, 95 Mpa



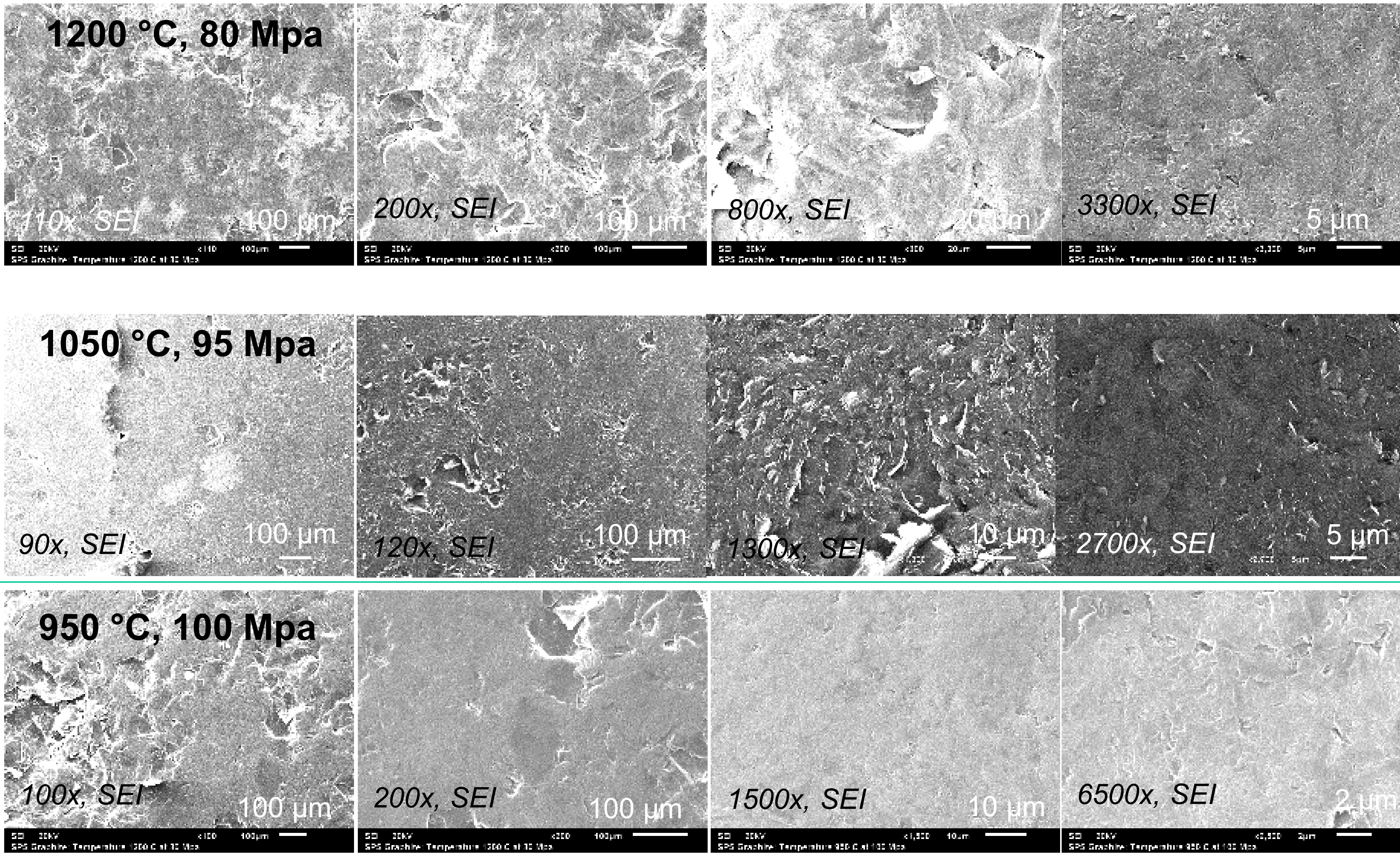
950 °C, 100 Mpa



Difficult to distinguish sintered portions in the fractured surfaces

SEM of Polished Sintered Pellets

- + same electrical bias + high temperature + pressure



Higher pressures are key to assisting sintering a solid where the temperature is within 250° C