LLNL-TR-869785

LAWRENCE LIVERMORE NATIONAL LABORATORY

Production of Readily Compressible Dies for the Enhanced Sintering of Solids (PRESS) Preliminary Investigations

M. Jancich, H. Charalambous, P. W. F. Evans, J. Rivera

September 27, 2024

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

Production of Readily Compressible Dies for the Enhanced Sintering of Solids (PRESS) Preliminary Investigations

Maxwell Jancich

Advised by Dr. Harry Charalambous

Lawrence Livermore National Laboratory

Prepared for the US Department of Energy

Abstract

Non-oxide ceramics, which consist of predominantly carbides, borides, and nitrides, are of great interest to modern engineering because of their resistance to extreme conditions. Properties of such materials include high temperature resistance, high hardness, chemical resistance, and high fracture toughness. However, the main method for manufacturing parts of these materials is by machining cylindrical billets to the desired geometry. Not only does this produce waste, but the cost of machining is high since the part materials are of such high hardness. This method is used because these non-oxide ceramics must be sintered to high density using simultaneous heat and pressure within a hot-pressing unit. These units are inherently restricted to cylindrical geometries. A proposed way to expand the capabilities of a hot-press is by using intermediate compressible dies. This method consists of surrounding a ceramic part green body with a material that will shrink at the same rate as the part and survive the hot-pressing conditions. At the end, the compressible die material would be removed leaving a nearly net shaped hot-pressed part. In this study, graphite powder was investigated as the compressible die material with its shrinkage rate being controlled by particle size mixing. Both ceramic materials and graphite were then cast into parts and compressible dies respectively to show the feasibility of the compressible die hot-pressing method.

I. Introduction

A. Motivation

As human engineering progresses, materials that can withstand more extreme conditions are required. Some technologies are specifically halted because there are not yet materials that can keep up with the intended function. Advanced ceramics is one group of materials that aims to fill material gaps that pertain to temperature resistance, hardness, chemical resistance, and high fracture toughness. While many common ceramics are of the metal-oxide type, non-oxide ceramics such as carbides, borides, and nitrides often have superior properties[1] and melting temperatures in excess of 2000°C. The materials discussed in this report are detailed in Table 1.

Table 1: Non-oxide ceramics and composites of interest

Material	**Properties**	**Applications**
ZrB_2/SiC 80/20 vol%[2]	Oxidation resistance, high thermal and electrical conductivity	Heat exchangers, nozzles
B_4C [3]	High hardness, neutron absorption	Armor, cutting tools, nuclear plant radiation shielding
SiC/Al_2O_3 95/5 vol% [4]	High thermal conductivity, low thermal expansion	Cutting tools, armor

However, the superior properties of non-oxide ceramics make them more difficult to process. The high hardness can make machining costly, up to 70% of the entire manufacturing process. Furthermore, pressure assisted sintering in an inert atmosphere is needed for many non-oxide ceramics[1]. This eliminates the popular method of pressure-less sintering if the properties cannot be sacrificed by using sintering aids.

B. Proposed method

This leaves the need for a manufacturing process that can easily sinter near net shape green bodies of non-oxide ceramics using pressure. A proposed method is the production of readily compressible dies for the enhanced sintering of solids (PRESS)[5]. This method proposes the use of an intermediate compressible medium surrounding a ceramic green body within the die of a hot press. In theory, this medium will match the compression of the ceramic green body while it is hot-pressed and be able to be removed at the end. This proposed method is superior to using rigid molds within a hot-press since it would not lead to density gradients within the part and can be used for a wider range of geometries. Figure 1 details the PRESS method.

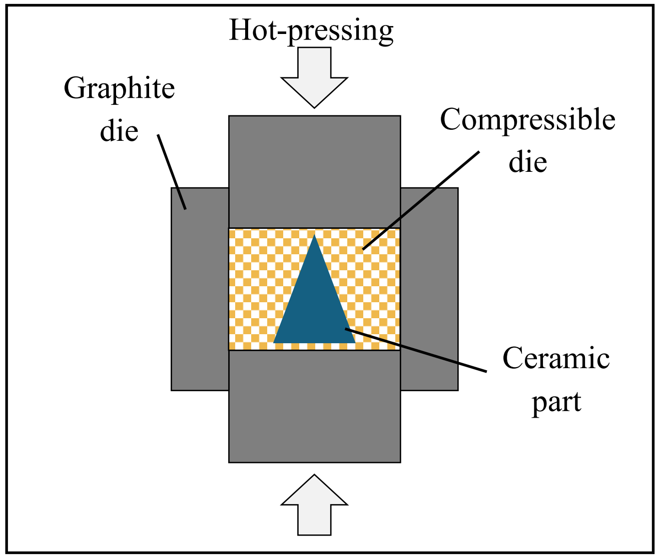


Figure 1: PRESS method; depicts a standard hot-pressing die filled with an intermediate compressible die and ceramic part

For the intermediate compressible material, graphite powder was selected as an initial candidate due to its low hardness and thermal stability. These properties would allow the graphite to conform around the ceramic green body while it sintered and be easily removed at the end.

C. Overview

The first topic investigated in this report is the tunable compressibility of graphite. For the PRESS method, it is important for the intermediate compressible die to shrink at the same rate as the ceramic part within the hot-press to avoid density gradients. Since different part materials will shrink by different amounts due to hot-pressing, a way for adjusting the total shrinkage of the intermediate die is needed. In theory, the packing density of a powder can be modified by size mixing. An ideal packing mixture would contain small particles filling the gaps between larger particles[6].

The next topic is the casting of ceramic and graphite green bodies. For consistent data to be acquired regarding the PRESS method, a reliable way to make ceramic and graphite green bodies was needed. By testing the limits of casting each material, insights could be gained on how to progress with the PRESS method. When upgrading the casting to non-cylindrical shapes, a conical geometry was chosen since it is particularly difficult to sinter without using the PRESS method. This is because when using a rigid die, the edges of the cone would reach high density before the central axis and the part would become locked in the die.

II. Methods

A. Compressibility of Graphite

The hypothesis that mixing graphite powders of different size distributions would affect the compressibility[6] was tested by creating a series of mixtures and plotting their displacement as a function of pressure. Two graphite powders were used: a 400-1200 nm dispersion (referred to as fine graphite), and a 325-mesh graphite (referred to as coarse graphite). The mixtures are referred to in terms of their mass percentage of fine graphite (e.g. 20% fine contains 20% fine graphite and 80% coarse graphite by mass). Images of the source powders can be seen in Figure 2. For the tests, 2 grams of each mixture was loaded into a steel die set with diameter 20mm. Initial height was tabulated and displacement from this height was measured using a dial gauge indicator at a series of pressures in a hydraulic press. Density was calculated while in the die by calculating volume using the displacement value and dividing the input mass by that value.

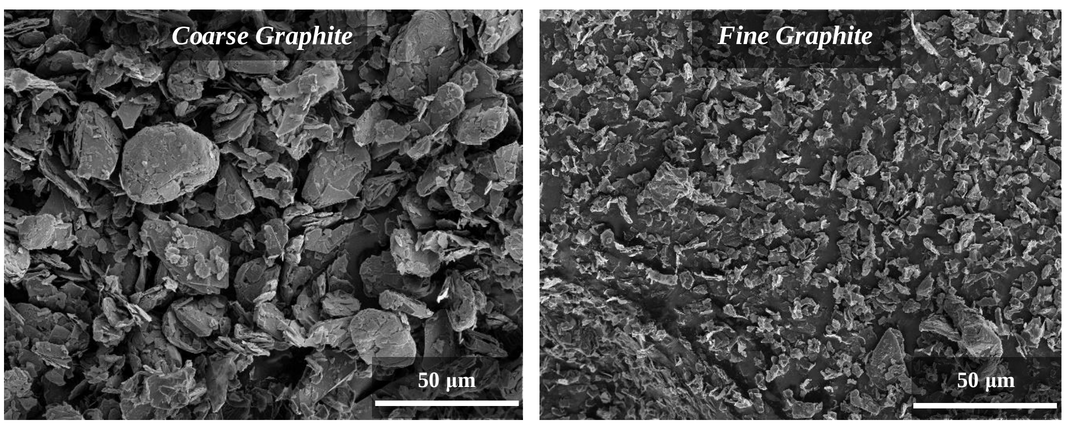


Figure 2: SEM of graphite powders

B. Casting

To manufacture near net shape ceramic parts of high density, near net shape green bodies were first required. For this study, both graphite and the part material green bodies were made by suspending powder in a solution of water and a dispersant, polyethylenimine (PEI) MW 25k[7]. For the casting of the ceramic part materials, the weight percent of PEI (PEI mass/ceramic mass) was minimized to prevent organic contamination. The solids loading (powder volume/water volume + powder volume) was maximized to prevent shrinkage/cracking upon drying and to raise green body density. The suspension recipes used are reflected in Table 2. The PEI weight percentage of 2% was selected for ZrB_2/SiC and scaled to the other materials to keep volume percent consistent.

Table 2: Ceramic part material casting recipe

Material	Solids Loading	Weight % PEI
ZrB_2/SiC 80/20 vol%	61%	2%
B_4C	60%	4.4%
SiC/Al_2O_3 95/5 vol%	55%	3.4%

For the casting of graphite green bodies, solids loading was again maximized to reduce shrinkage/cracking and increase density. Maximizing green body density was particularly important for graphite since their density percentage trailed that of the ceramic green bodies by a large margin. Approximate density matching would help achieve matching shrinkage rates under pressure. The maximum castable solids loadings for each graphite mixture are shown in Table 3.

Table 3: Maximum achieved solids loading for graphite mixtures

Fine graphite %	Solids Loading
100	26.2%
90	31.6%
80	32.1%
50	33.7%
30	35.6%
20	34.7%
10	34.0%
0	36.6%

To make each slurry, the water and PEI were first mixed to uniformity using a planetary mixer. The powder was then added and mixed thoroughly in the planetary mixer. To find the maximum castable solids loading of each material, a slurry was made with a solids loading much higher than the expected solids loading and incrementally diluted with water until it reached a uniform consistency that could be transferred into the mold. Since the PEI slurries exhibited shear thinning behavior, a castable slurry was defined as one that would begin to pour when sufficiently agitated. Each mixture was poured into a silicone mold with three puck shaped recesses (20mm diameter, 10mm height). This mold was fit into a planetary mixing cup and briefly mixed and defoamed (centrifuged). This method, centrifugally assisted packing[8], allowed for the shear thinning slurry to infiltrate the mold and remove air pockets. The molds were then dried in air for several hours and left in an 80°C drying oven overnight. The resulting pucks were removed and lightly sanded flat to measure their approximate volume to calculate density.

C. Casting of non-cylindrical geometries

Casting of simple, non-cylindrical geometries could also be done using silicone molds. To investigate the hot-pressing of a cone using the PRESS method, molds for cones were made for the ceramic part materials and molds for cone-negative dies were made for the graphite. These molds could be easily made by pouring silicone around positives made using a resin stereolithography printer. Figure 3 depicts some of such molds.

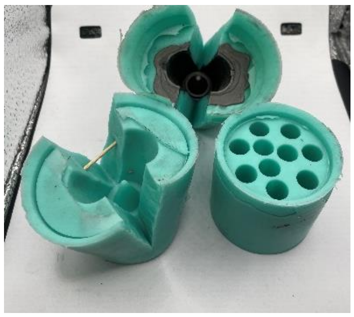


Figure 3: Cone-negative molds (left, top); fracture strength sample mold (right; not included in this report)

III. Results

A. Compressibility of graphite

Qualitatively, it was noticed that the mixtures containing a majority fine graphite were fluffy and occupied more volume than the coarser graphite mixtures at the same mass. This was reflected in the density measurements. The relative density as a function of pressure can be seen in Figure 4. At the low-pressure end, it is apparent that the initial packing density of graphite could be tuned by size mixing. It can also be noticed that the mixtures began to converge on a common maximum relative density as the pressure increased. Using the initial and final densities of each mixture, the shrinkage percentage could be calculated (100 × [final density – initial density] / initial density). Figure 5 shows how the shrinkage percentage varied across the mixtures.

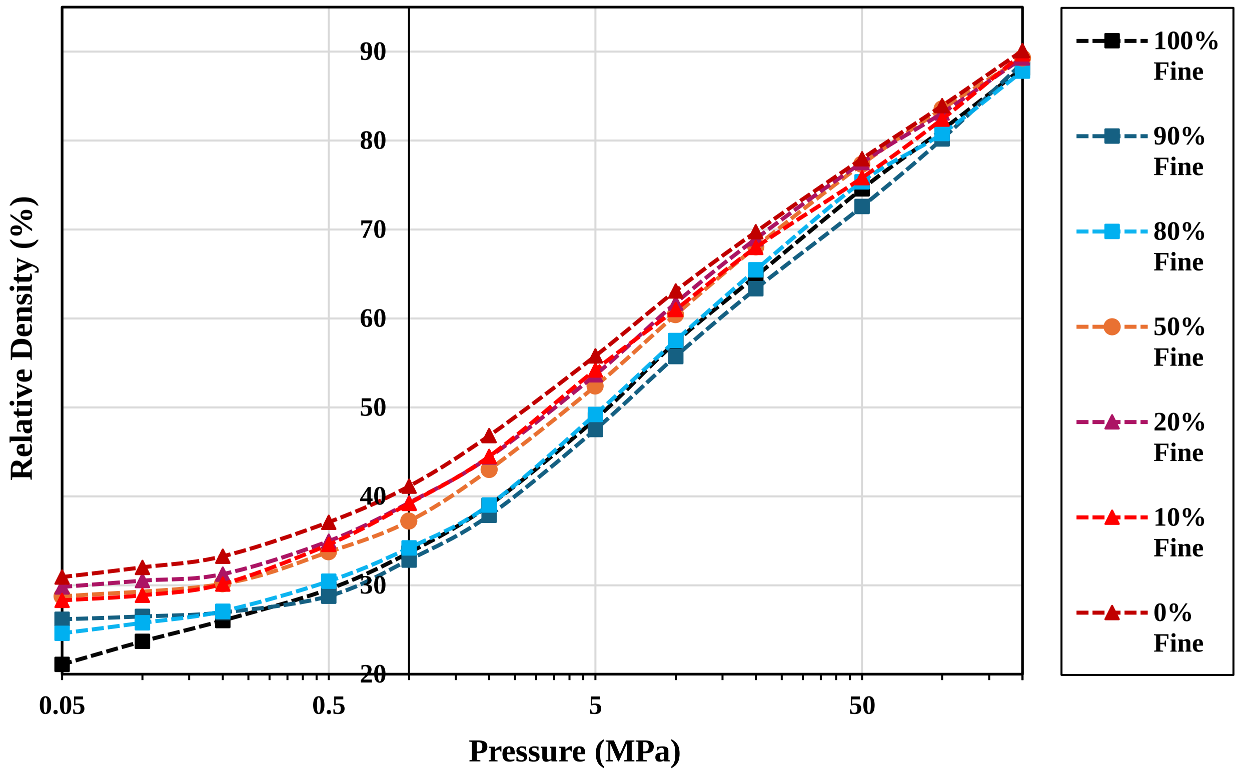


Figure 4: Density Percent of various graphite mixtures as a function of pressure measured in a hydraulic press (x-axis log scale)

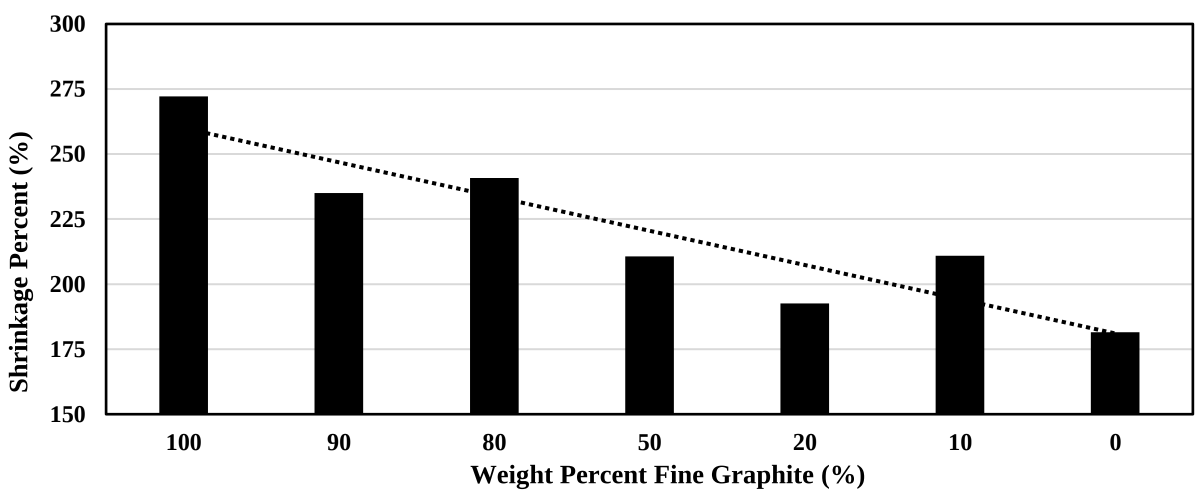


Figure 5: Shrinkage percentage 0.1MPa to 200MPa (line shows approximate trend)

B. Casting

From the graphite casting trials, it was noticed that higher coarse graphite content led to higher maximum solids loading. However, increasing the solids loading provided diminishing returns in green density once the solids loading rose above 34%. This trend can be seen in Figure 6; the green density flatlines as the solids loading increases. This requires further investigation by more extensive testing.

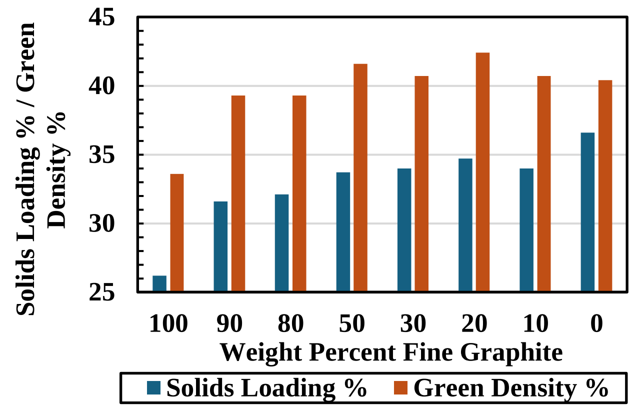


Figure 6: A comparison of solids loading and the resulting green density for the graphite casting series

The ceramic slurries proved to be easier to cast than the graphite. This was because the graphite resulted in a slurry with a foam-like consistency rather than the ceramic slurries which had consistencies of viscous liquids. Furthermore, the solids loading was able to be pushed to values near 60% for each ceramic material versus 34% for the graphite. The green density of the cast ceramic pucks as well as the coarse graphite puck can be seen in Figure 7.

Material	Green Density (relative)
ZrB_2/SiC 80/20 vol%	62%
B_4C	62%
SiC/Al_2O_3 95/5 vol%	58%
Coarse Graphite	40%

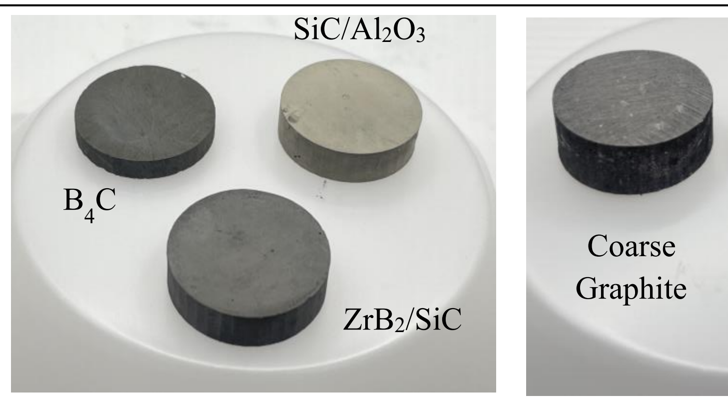


Figure 7: Green density achieved for each material (left); images of green body pucks

C. Cone system casting

Cones of height 26mm and diameter 13mm were able to be cast using the same recipes discussed in the methods. These green body cones displayed high durability during the demolding and handling process. Coarse graphite with 34% solids loading was used to cast the cone-negative dies. The graphite green bodies did not show as much durability as the ceramic counterparts, but they were still able to be demolded and handled. These cast green bodies are depicted in Figure 8.

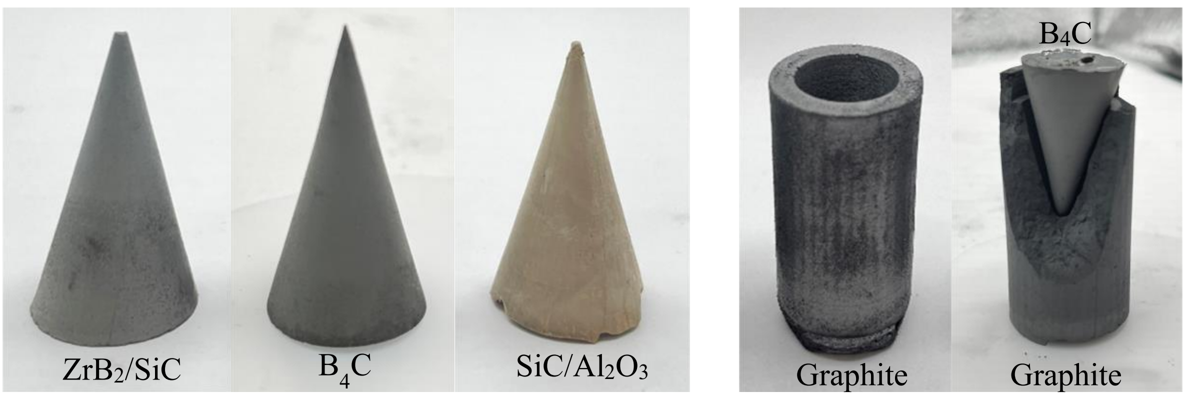


Figure 8: Cast green ceramic cones (left); cast graphite cone-negative and fractured graphite cone-negative with B_4C cone inside (right)

IV. Discussion

A. Compressibility of graphite

With the graphite powders used in this experiment, it was shown that the cold compaction of graphite powder could be tuned by altering the particle size distribution. More specifically, the coarse graphite (325 mesh) yielded the highest initial packing density, and the fine graphite (400-1200nm) yielded the lowest. The ratios in between yielded intermediate densities. Although it was predicted that the highest initial packing density would result from a mixture containing mostly coarse and a small percentage of fine, the actual result can be explained by the fact that the source graphite powders were not uniformly sized but were already a mixture of a wide variety of sizes.

Under cold pressing conditions, the graphite with the lowest shrinkage percentage, the coarse graphite (325 mesh), exhibited approximately 125% shrinkage from initial packing to 30MPa (density at 30MPa was individually tested since this value was settled upon after the cold compression series was performed). This value was promising since the shrinkage percentage of the discussed part materials ranged from 120-165% (calculated from hot-pressing at 30MPa). However, these results would prove to be misleading because the assumption was made that graphite does not sinter under hot-pressing conditions and the compression behavior could be strictly studied via cold pressing. This was discovered to be partially untrue, leading to a new series of graphite compression tests under hot-pressing conditions which will be detailed in another report.

B. Casting Study

The ceramic part materials were able to be cast into high density, high solids loading pucks and cones using the investigated recipe. The relative green densities even exceed the relative densities achieved by cold pressing at 100MPa. The graphite proved to be more difficult to cast using the initial recipe, not turning into a uniform slurry until the solids loading dropped below 36%. The achieved relative green density was much lower than the density achieved by cold pressing at 100MPa. The graphite recipe requires further research and development to become optimal. The recipes, densities, and comparative cold pressed densities at 100MPa are summarized in Table 4.

Table 4: Casting summary and density comparison

Material	PEI (wt.%, vol.%)	Solids Loading	Cast Density	Cold-Pressed Density 100MPa
ZrB_2/SiC	2%, 8%	62%	62%	56%
B_4C	4.4%, 8%	60%	62%	54%
SiC (+Al_2O_3)	3.4%, 8%	54%	58%	52%
Graphite	10%, 16.5%	26-37%	34-42%	80-84%

Cast samples were also prepared for strength testing which will be detailed in a following report. For these tests, the graphite parts were tested as a function of PEI weight percent. During the production of these parts, it was noticed that increasing the amount of PEI created uniform graphite slurries at much higher solids loading values than the initial recipe. This was an indication that further adjustments and trials should be performed regarding the PEI graphite slurry recipe.

C. Non-cylindrical geometries

Both cone and cone negatives were able to be cast such that they could be hot pressed as one unit. Although the compressibility did not exactly match, the travel distance problem would still be solved with minor part geometry distortion.

V. Conclusion

The work detailed in this report was able to illustrate that key aspects of the PRESS method were plausible on a small scale. It was first shown that the compressibility of graphite powder could be tuned by size mixing. This was followed by the successful casting of the ceramic materials of interest ZrB_2/SiC (80/20 vol%), B_4C, and SiC/Al_2O_3 (95/5 vol. %) using a simple, 3 ingredient recipe with low organic additives. Graphite was also able to be cast using a similar, simple recipe. The casting recipes were able to be applied to the geometry of interest, the cone, resulting in successfully cast ceramic green body cones and graphite compressible dies. According to these results, the PRESS method should be investigated further by extensive hot-pressing trials, further geometry complication, and size scaling.

VI. Acknowledgements

I would like to thank Harry Charalambous, Peter Evans, and Jesus Rivera for their mentorship and support during this internship. This work was supported in part by the U.S. Department of Energy, Office of Science, Office of Workforce Development for Teachers and Scientists (WDTS) under the Science Undergraduate Laboratory Internships Program (SULI).

This work was funded by Laboratory Directed Research and Development (24-FS-020) initiative under Lawrence Livermore National Laboratory. Released under LLNL-TR-869785. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

VII. References

[1]Y. Lakhdar, C. Tuck, J. Binner, A. Terry, R. Goodridge, “Additive manufacturing of advanced ceramic materials,” Progress in Materials Science, 116, 2021, p. 100736.

[2]S. C. Zhang, G. E. Hilmas, W. G. Fahrenholtz, “Mechanical properties of sintered ZrB2–SiC ceramics,” Journal of the European Ceramic Society, 31: 5, 2011, pp. 893-901.

[3]V. Domnich, S. Reynaud, R. A. Haber, M. Chhowalla, “Boron Carbide: Structure, Properties, and Stability under Stress,” Journal of the American Ceramic Society, 94, 2011, pp. 3605-3628.

[4]M. Parchovianský, D. Galusek, J. Sedláček, P. Švančárek, M. Kašiarová, J. Dusza, P. Šajgalík, “Microstructure and mechanical properties of hot pressed Al2O3/SiC nanocomposites,” Journal of the European Ceramic Society, 33: 12, 2013, pp.2291-2298.

[5]Harry Charalamobous, unpublished work

[6]C.L. Martin, D. Bouvard, “Isostatic compaction of bimodal powder mixtures and composites,” International Journal of Mechanical Sciences, 46: 6, 2004, pp.907-927.

[7]A. Diaz-Cano, R. W. Trice, J. P. Youngblood, “Stabilization of highly-loaded boron carbide aqueous suspensions,” Ceramics International, 43: 12, 2017, pp. 8572-8578.

[8]Jesus Rivera, Qirong Yang, Christian G. Bustillos, Swetha Chandrasekaran, Amy Wat, Elizabeth M. Sobalvarro, Marcus A. Worsley, Andrew J. Pascall, Joshua D. Kuntz, “Mechanical responses of architected boron carbide-aluminum lattice composites fabricated via reactive metallic infiltration of hierarchical pore structures,” Materials Today Communications, 37, 2023, p. 107550.

Production of Readily compressible dies for Enhanced Sintering of Solids (PRESS)

Summer SULI Presentation

Maxwell Jancich
Advised by Harry Charalambous, Jesus Rivera, Peter Evans

July 16, 2024

Lawrence Livermore National Laboratory

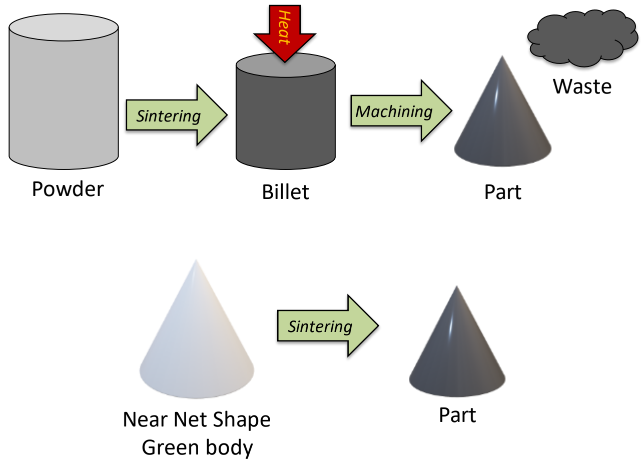
Abstract

Non-oxide ceramics are of great interest to modern engineering because of their properties which include high temperature resistance, high hardness, chemical resistance, and high fracture toughness. However, the main method for manufacturing parts of these materials is by machining cylindrical billets to the desired geometry. Not only does this produce waste, but the cost of machining is high since the part materials are of such high hardness. This method is used because these non-oxide ceramics must be sintered to high density using simultaneous heat and pressure within a hot-pressing unit. These units are inherently restricted to cylindrical geometries. A proposed way to expand the capabilities of a hot-press is by using intermediate compressible dies. This method consists of surrounding a ceramic part green body with a material that will shrink at the same rate as the part and survive the hot-pressing conditions.

MSD

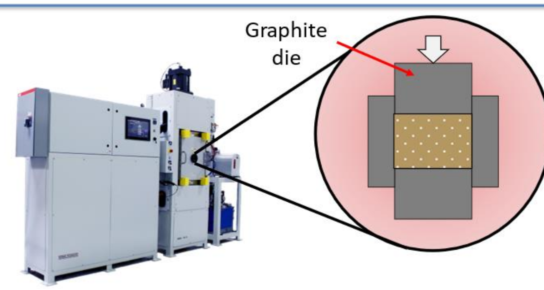
Near-Net Shaping

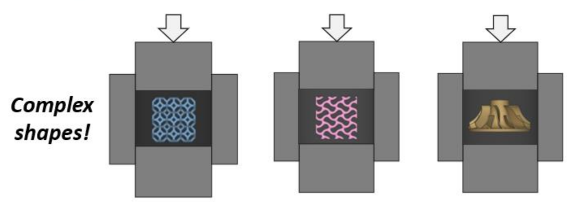
- Problem: Hard non-oxide ceramics have extremely high machining overhead time and costs
- Solution: **Near-net shaping**



Hot pressing of high-density, hard-to-sinter ceramics

- Hot pressing is the standard for high density parts
  - Problem: Rigid dies limit part geometry (travel distance problem)
- **PRESS** unlocks new possibilities for hot pressing
  - Compressible intermediate material accommodates variable thickness part



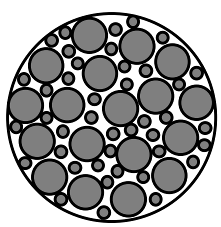


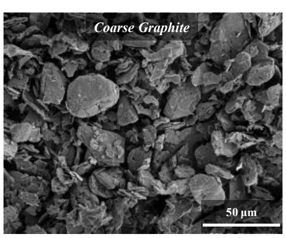
Materials and Applications

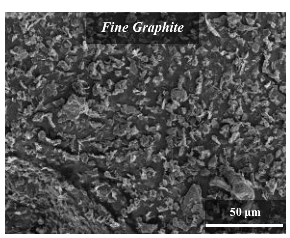
	Part or Die	Properties	Some applications
ZrB_2/SiC (80/20 vol%)	Part	Excellent oxidation resistance, high thermal and electrical conductivity	Heat exchangers, nozzles
B_4C	Part	High hardness, high neutron absorption	Armor, cutting tools, nuclear plant radiation shielding
SiC (+ 5 vol% Al_2O_3)	Part	High thermal conductivity, low thermal expansion	Cutting tools, armor
Graphite	Die	Highly deformable, thermally stable, and non-sintering	Graphite dies and heating elements

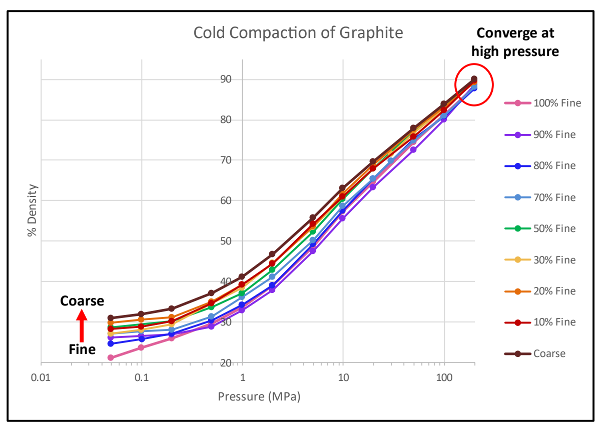
Graphite (cold) pressing study

- Theory: Size mixing allows tunable initial packing
  - Fine Graphite (0.4-1.2μm)
  - Coarse Graphite (325 mesh)









Gel casting strategy

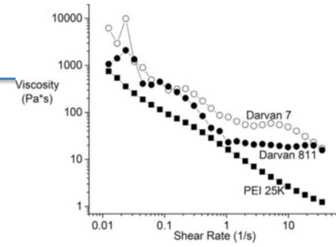
Gel-casting with Polyethylenimine (PEI) 25k

- simple recipe (PEI + H_2O + ceramic powder)
- minimal organic additives (2 -5 wt%)
- low viscosity at high solids loadings
- tough green bodies (Instron tests pending)

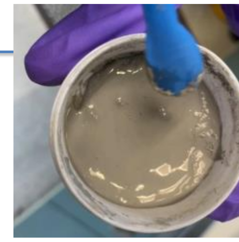
Centrifugally assisted packing (CAP)

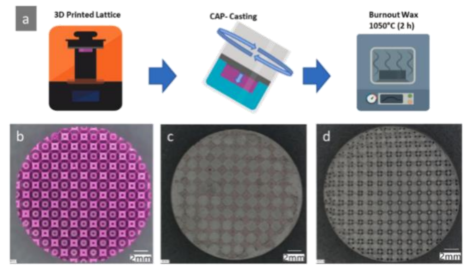
- Centrifugal motion applies substantial shear thinning force
- Pack material into narrow cavities (i.e. voids in lattices)

Goal: Strong, crack-free, and dense.



Diaz-Cano, A., R.W. Trice, and J.P. Youngblood, *Stabilization of highly-loaded boron carbide aqueous suspensions.* Ceramics International, 2017.**43**(12): p. 8572-8578.

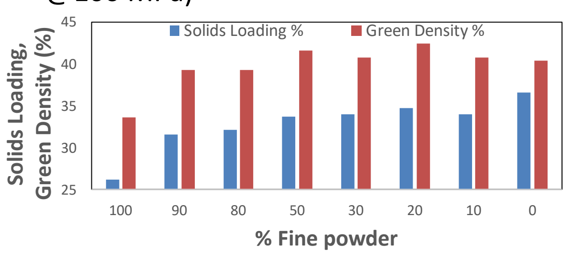




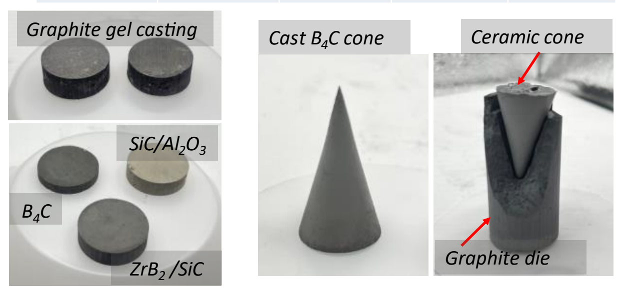
Rivera, J., et al., *Mechanical responses of architected boron carbide -aluminum lattice composites fabricated via reactive metallic infiltration of hierarchical pore structures.* Materials Today Communications, 2023.**37**: p. 107550.

Gel casting results

- Graphite needs high PEI vol% (soft, brittle)
- Coarser graphite = higher solids loading, same green density (except 100% fine)
- Gel casting (+CAP): dense ceramic green bodies (more dense than pressed pellets @100 MPa)

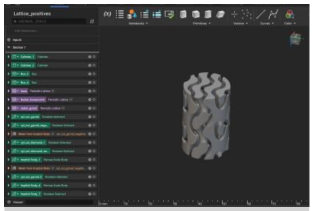


Material	PEI (wt%, vol%)	Solids Loading	Cast Density	Pressed Density
ZrB_2/SiC	2%, 8%	62%	62%	56%
B_4C	4.4%, 8%	60%	62%	54%
SiC (+Al_2O_3)	3.4%, 8%	54%	58%	52%
Graphite	10%, 16.5%	26-37%	34-40%	80-84%



Design and casting/printing of mold templates

- Design (nTopology, SolidWorks)
- SLA printing – high resolution, highly complex geometries
- Silicone molds – fill the spaces needed, easily demoldable, mirror resolution of SLA prints



Design (nTopology)

SLA Print

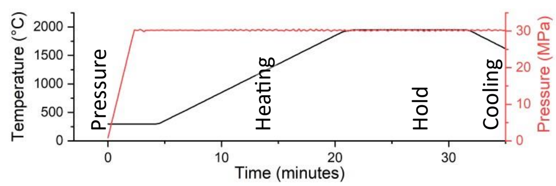
Gel cast infill

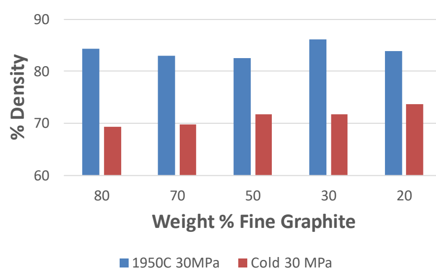
Burnout/ Pre-sinter

Next steps: Pack the lattice with graphite and hot press, then burn off graphite

Graphite (hot) pressing study

- Direct current sintering (DCS)
  - High sample throughput
  - Can emulate traditional hot press by insulating part from current with hBN coated spacers
- Graphite hot pressing
  - At the sample pressure, graphite reaches higher density at high temperature
- Full analysis pending…

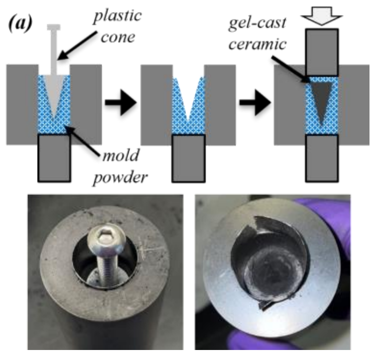


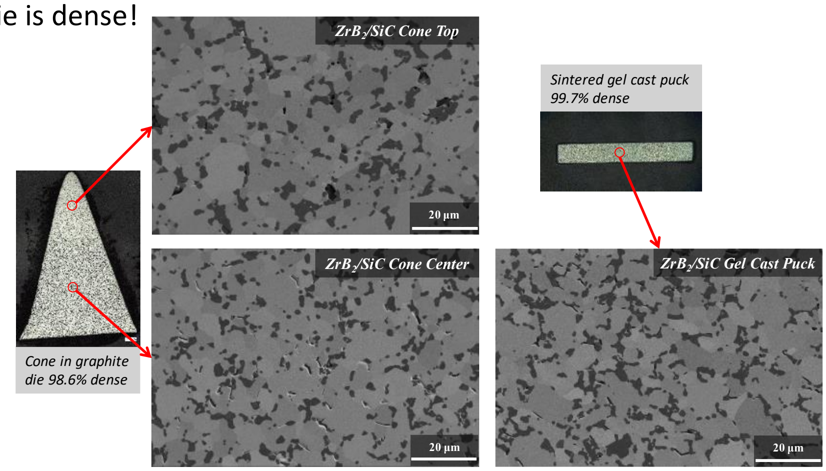


Puck	Density
ZrB_2/SiC	99.7%
B_4C	96.6%
SiC/ Al_2O_3	97.6% *powder

Hot pressing of flat puck and cone in mold

- Cone in graphite powder die is dense!
- Slight density gradient

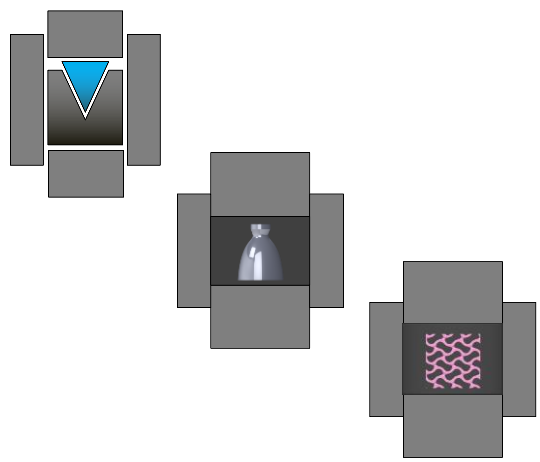




What's next?

- Sinter a cast cone/die assembly
- PRESS ceramic nozzle
- PRESS lattice – extremely complex geometry
- PRESS B_4C and SiC cones

- Complete DCS compression study for all part (ZrB_2/SiC, B_4C, SiC) and mold (fine to coarse graphite) materials



Questions?

Were you im**PRESS**ed?

This work was funded by Laboratory Directed Research and Development (24-FS-020) initiative under Lawrence Livermore National Laboratory. Released under LLNL-TR-869785. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE -AC52-07NA27344.

MSD

Lawrence Livermore National Laboratory

Sources

[1]Y. Lakhdar, C. Tuck, J. Binner, A. Terry, R. Goodridge, "Additive manufacturing of advanced ceramic materials," Progress in Materials Science, 116, 2021, p. 100736.

[2]S. C. Zhang, G. E. Hilmas, W. G. Fahrenholtz, "Mechanical properties of sintered ZrB2–SiC ceramics," Journal of the European Ceramic Society, 31: 5, 2011, pp. 893-901.

[3]V. Domnich, S. Reynaud, R. A. Haber, M. Chhowalla, "Boron Carbide: Structure, Properties, and Stability under Stress," Journal of the American Ceramic Society, 94, 2011, pp. 3605-3628.

[4]M. Parchoviansky, D. Galusek, J. Sedláček, P. Švančárek, M. Kašiarová, J. Dusza, P. Šajgalík, "Microstructure and mechanical properties of hot pressed Al2O3/SiC nanocomposites," Journal of the European Ceramic Society, 33: 12, 2013, pp.2291-2298.

[5]C.L. Martin, D. Bouvard, "Isostatic compaction of bimodal powder mixtures and composites," International Journal of Mechanical Sciences, 46: 6, 2004, pp.907-927.

[6]A. Diaz-Cano, R. W. Trice, J. P. Youngblood, "Stabilization of highly-loaded boron carbide aqueous suspensions," Ceramics International, 43: 12, 2017, pp. 8572-8578.

[7]Jesus Rivera, Qirong Yang, Christian G. Bustillos, Swetha Chandrasekaran, Amy Wat, Elizabeth M. Sobalvarro, Marcus A. Worsley, Andrew J. Pascall, Joshua D. Kuntz, "Mechanical responses of architected boron carbide-aluminum lattice composites fabricated via reactive metallic infiltration of hierarchical pore structures," Materials Today Communications, 37, 2023, p. 107550.