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Sandia National Laboratories

Exceptional service in the national interest

LCM Ceramic Material Development and Characterization

D. Cillessen (SNL) & S. Allan (Lithoz America)

SNL Team Members: R. Andersen, B. Kirkpatrick, M. Aragon, W. Davidson

Presented at the 2022 Additive Manufacturing Users Group

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Introduction

Dale Cillessen, P.E.

A Senior Member of the Technical Staff in the Applied Science Technology Maturation Department at Sandia National Laboratories in Albuquerque, NM. Dale is the engineering operational lead of Sandia's metal and ceramic printing facility. His research focuses on developing accurate, repeatable, structurally sound advanced manufactured components.

Shawn Allan

Started Lithoz America in 2017 in New York

BS Ceramic Engineering & Materials Science, Alfred University

MS Materials Science, Georgia Tech

Delivering unmatched Ceramic Additive technologies and materials. Developing sales, training, support, demonstration and development project capabilities for Lithoz in North America.

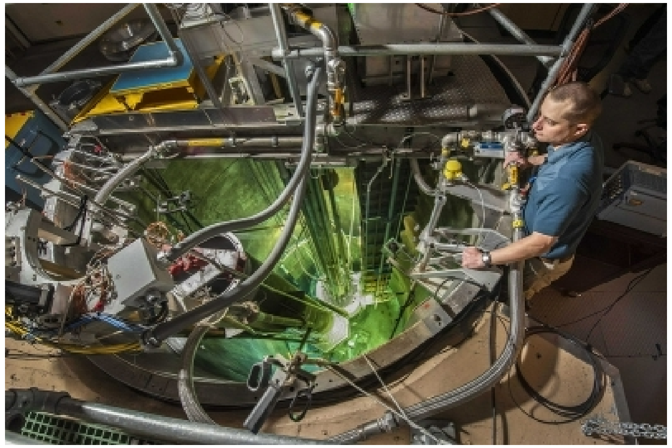
Outline/Agenda

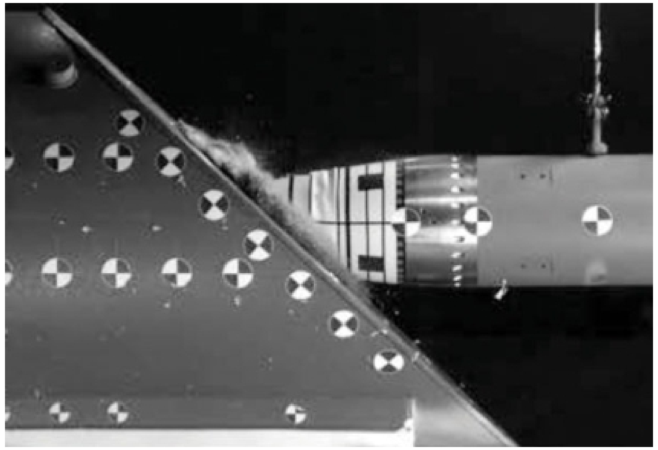
- Who is Sandia National Laboratories
- Motivation
- Developing and characterizing a glass-bonded alumina ceramic
- Using the characterized alumina to inform the design of an example component
- Dimensional characterization of the example component
- Developing and characterization of a molybdenum/alumina cermet
- Introduction to the Lithoz multi material DLP printer
- 2022 SNL and Lithoz America projects
- Conclusions

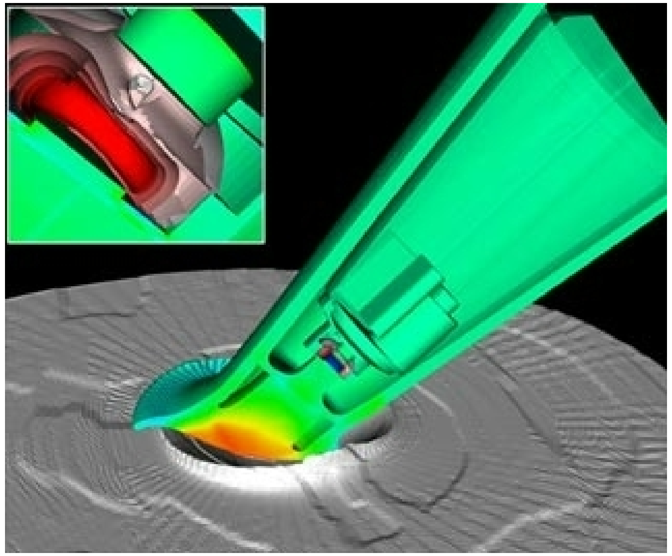
Who is Sandia National Laboratories

Sandia National Laboratories is one of the three National Nuclear Security Administrations research and development laboratories in the United States.

The primary mission is to develop, engineer and test the non-nuclear component of nuclear weapons.







Motivation

Pursuit of next level manufacturing technologies. Bridging the gap from development to production.

At Sandia National Laboratories Advanced Manufacturing Enables Rapid Product Realization.

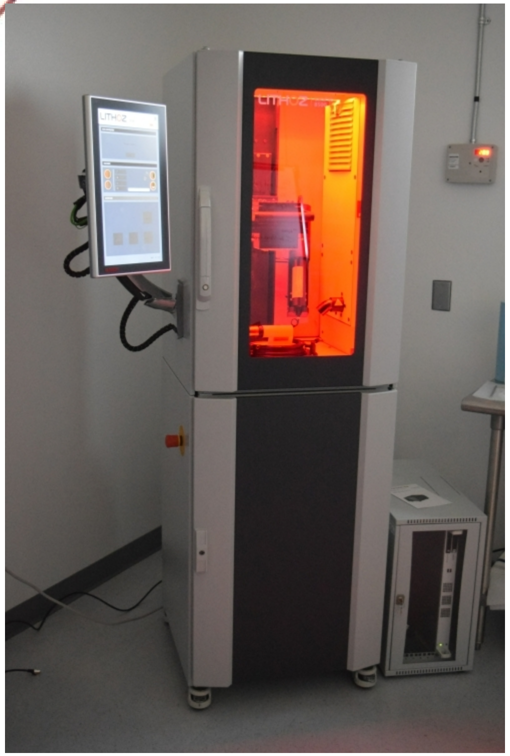
Ceramic Additive Manufacturing reduces development time, opens design opportunities, and provides rapid exploration of custom materials.

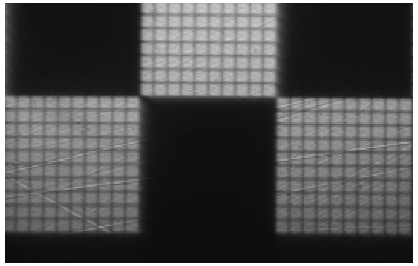
Expectations for Accelerating Product Realization: Digital Engineering

"Sandia National Laboratories (Sandia) has a responsibility to lead the Nuclear Security Enterprise (NSE) in Accelerating Product Realization (APR). Within APR there are four key focus areas: (1) Digital Engineering (DE), (2) risk-based project management, (3) technology insertion process, and (4) continuous improvement.

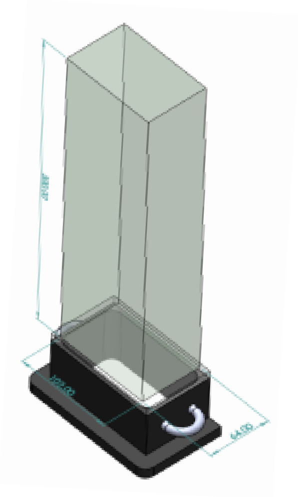
LCM Printing Process

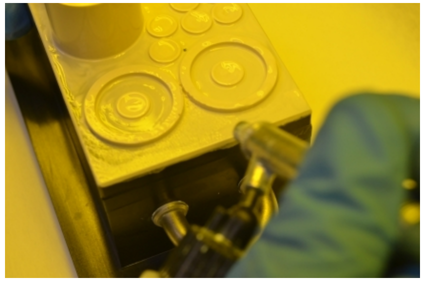
SNL Printing Facility





Resolution 40 micrometer X-Y, 10 micrometer (material dependent) Z

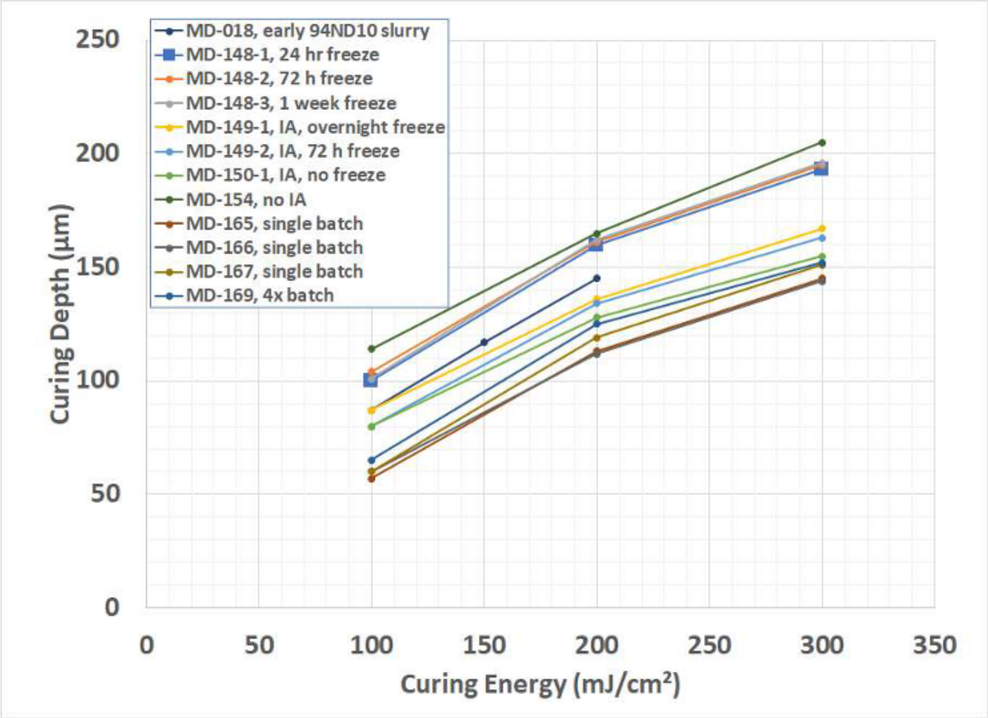




SNL's Alumina Ceramic Material

Sandia developed a Glass-Bonded Alumina ceramic. The glass-bonded material is 94% Al_2O_3, 1.5% MgO, 1.2% CaO, and 3% SiO_2 . The addition of Silica allows for processing at lower temperatures compared to pure Al_2O_3.

Conversion of the SNL material to a printable slurry.



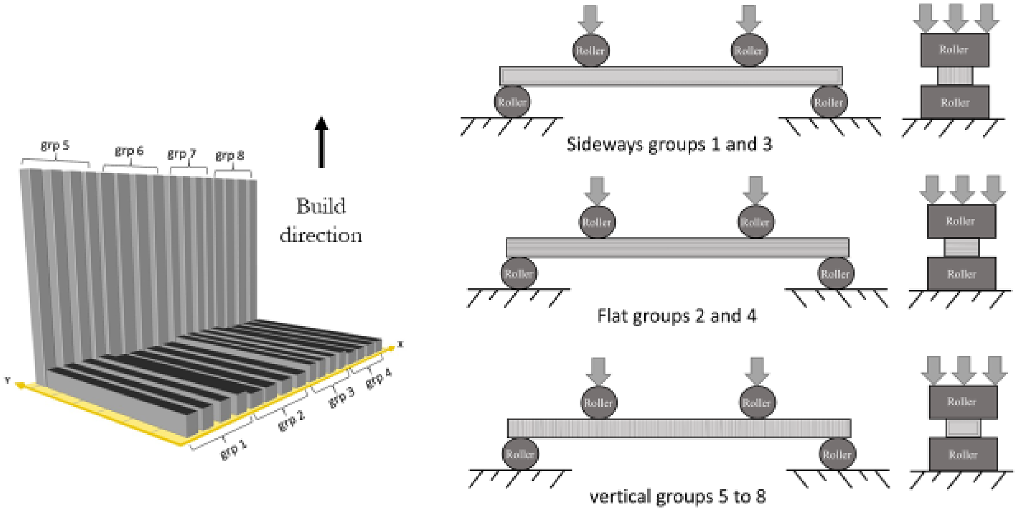
3.2. Job Parameters

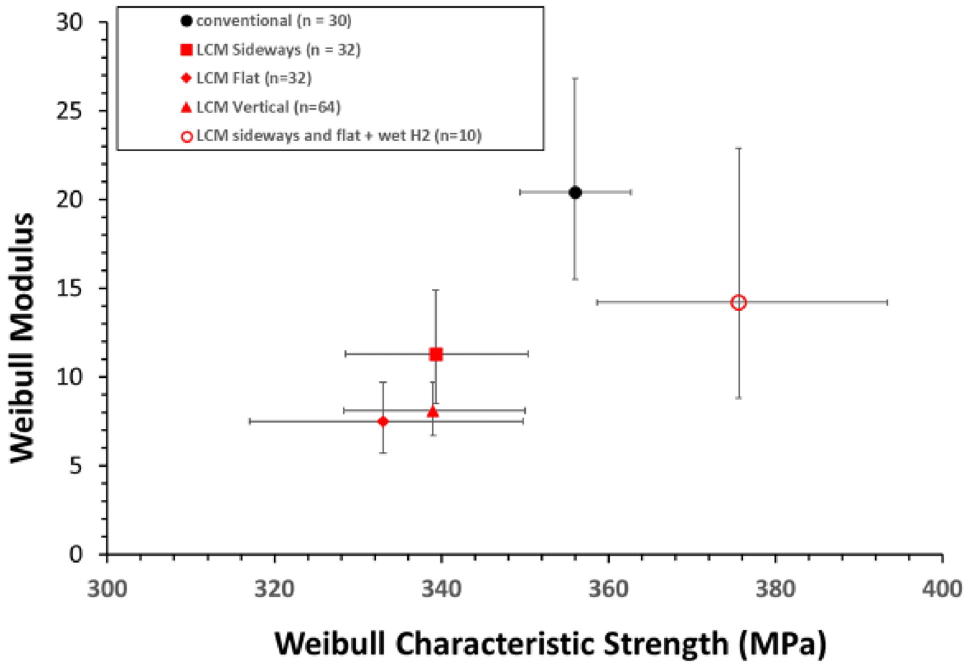
Parameter	*Standard Value*
Geometry	
Layer thickness [µm]	25
Support structure thickness [µm]	
Geometry corrections	
Contour offset [µm]	-40
Pixel alignment	Yes
Lateral (XY) shrinking compensation	1.203
Build direction (Z) shrinking compensation	1.353
Z curing depth compensation	Yes
Z curing depth compensation layers	1
Dispenser	
Dispensation correction	1.2
Dispensation correction support	1.4
Coat	
Angle of rotation start [rotations]	5
Angle of rotation general [rotations]	3
Rotation speed [°/s]	200
Contact	
Settling time start [s]	60
Settling time general [s]	10
Tilt up speed start [°/s]	5
Tilt up speed general [°/s]	10
Expose	

Highlights from Article

128 samples were tested in accordance with ASTM C1161-13 “four-point bend test” for flexural strength.

- Printed components meet the initial requirements for prototyping
- AM components have a decreased Weibull Moduli
  - Improvement following the Wet H_2 fire.
- All testing done on “As-Printed” Samples

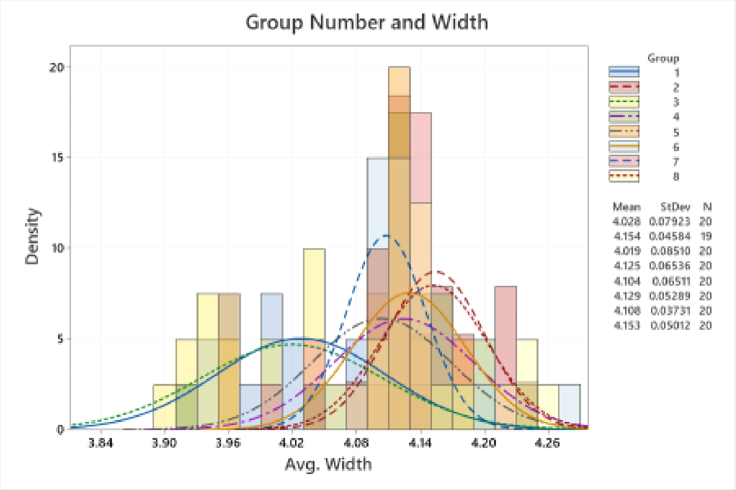


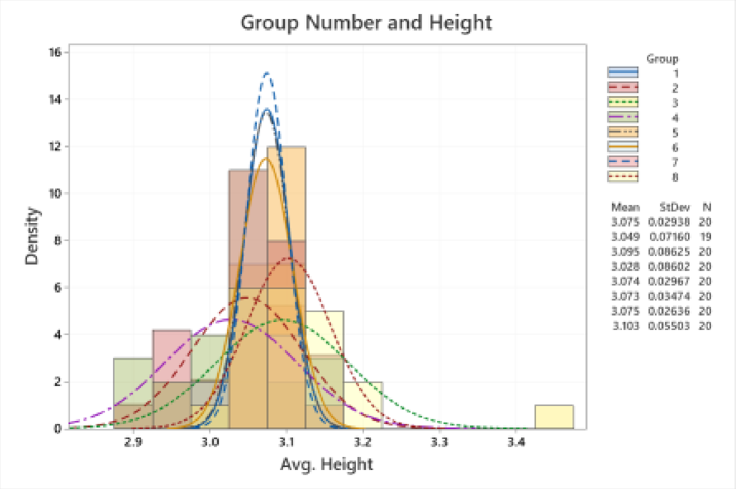


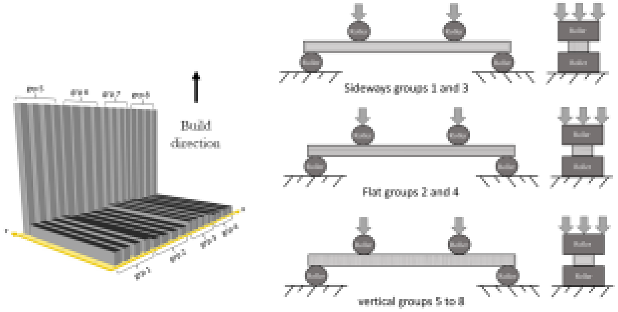
*D. Kammler, et al. Int. J. Appl. Ceram. Technol. 2021; 1-10. https://doi.org/10.1111/ijac.13968

Flex bars and Printing Accuracy

Print Orientation vs Dimension





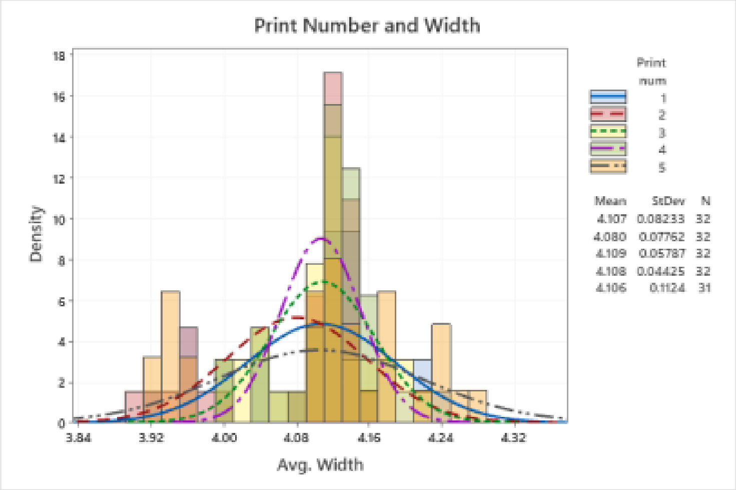


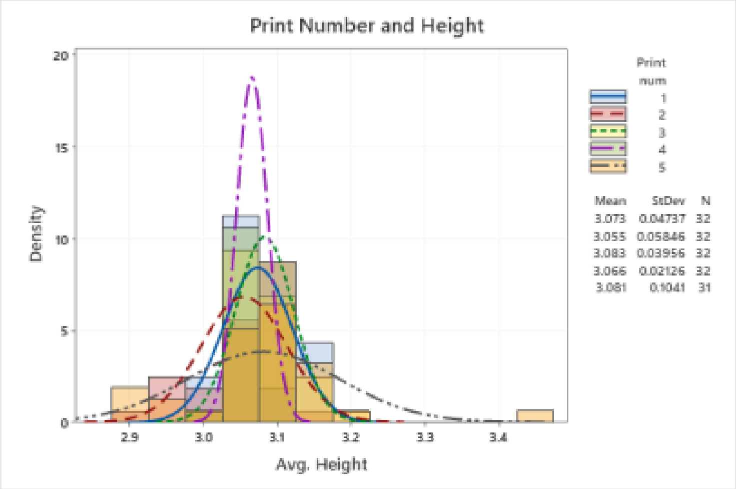
The histograms indicate the importance of appropriate scaling factors. XY and Z.

The vertical print orientation, groups 5 to 8 show to improve the dimensional characterization of the print.

Manufactured group 4, created the highest consistency between bars.

Print Number vs Dimension





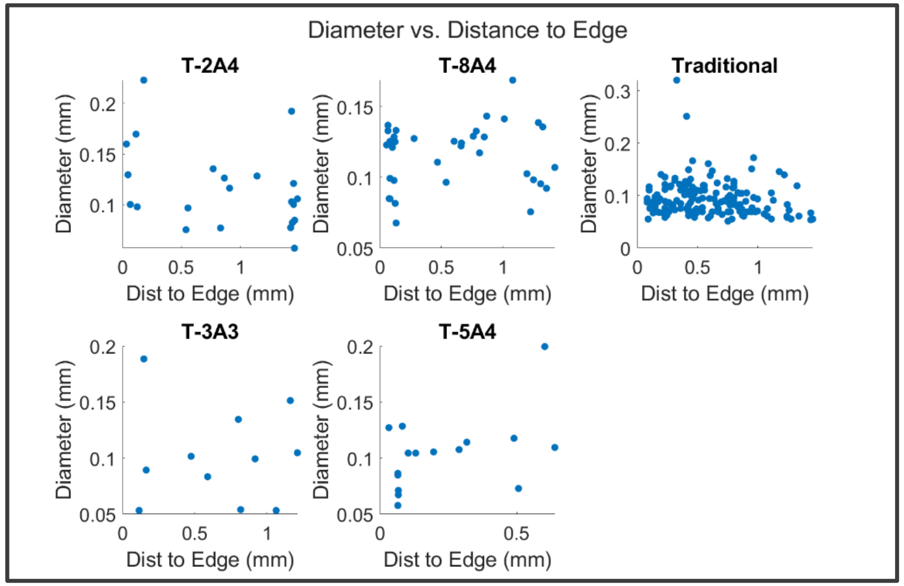
SNL Alumina Characterization Continued

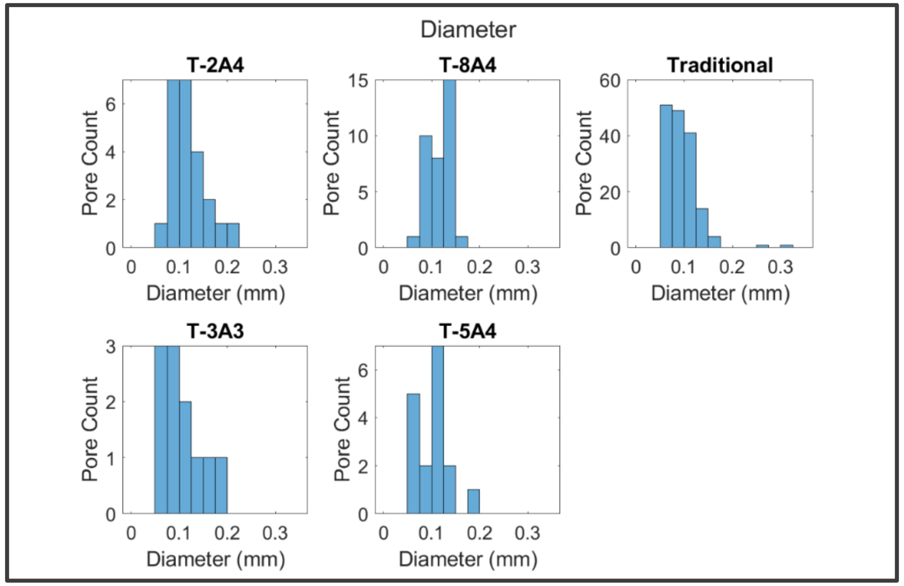
Computer Tomography (CT) of flexural bend samples.

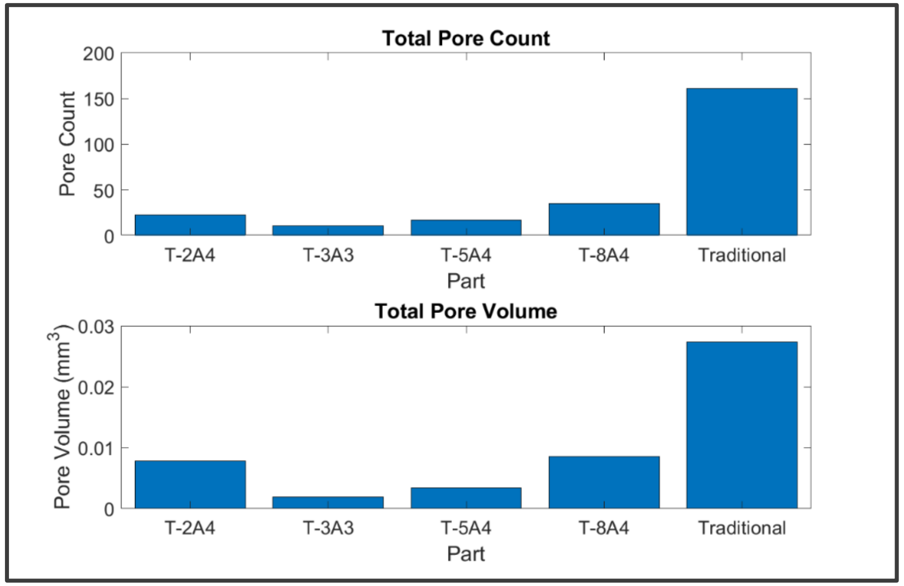
- Reduction of both pore volume and quantity with the additively manufactured samples. Likely due to the powdered material going through additional grinding process for AM.
- The results of the CT align with the slight increase in density observed for the additively manufactured components.

Density

Traditional = 3.73 (g/cm^3)   Printed = 3.732 (g/cm^3)



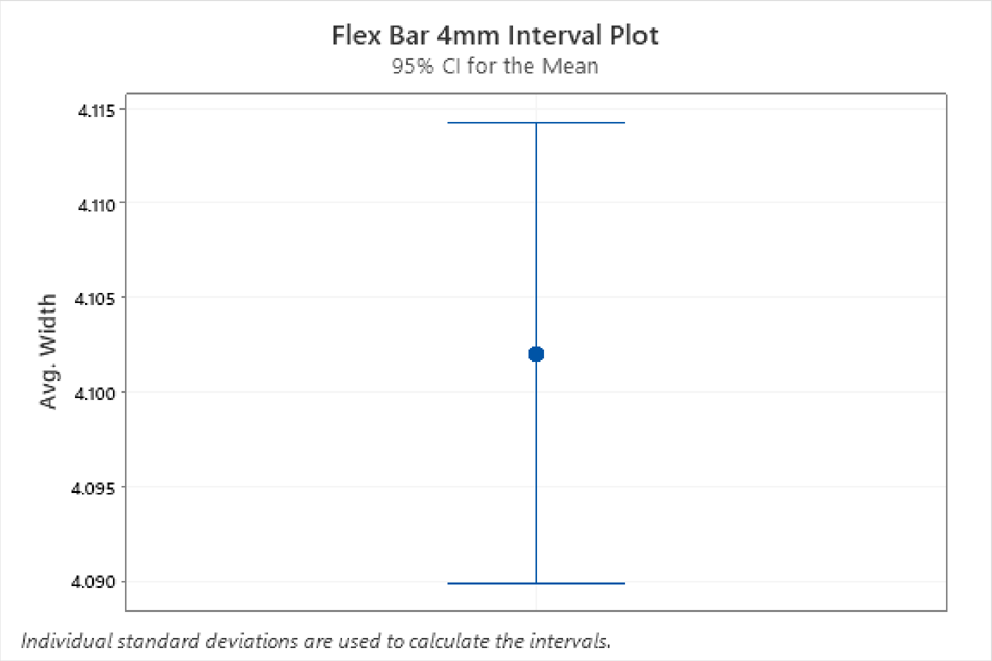


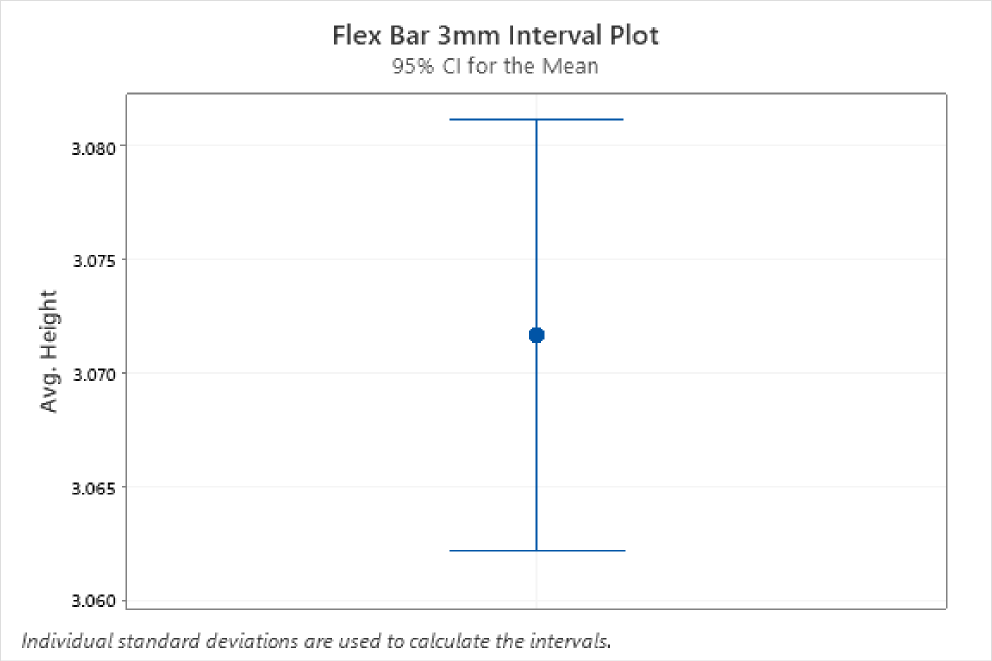


Results and Preparation for manufacturing components

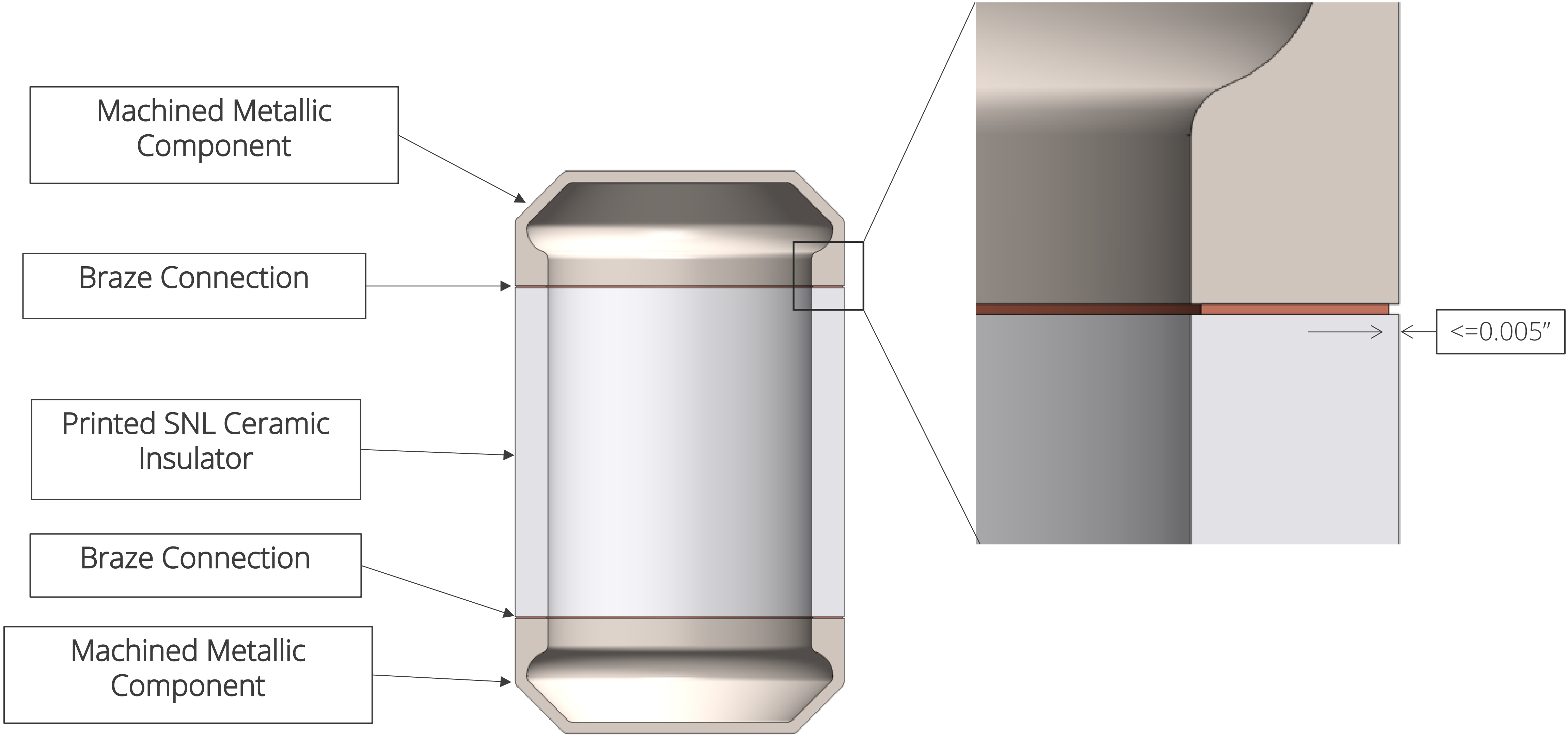
Characterizing the mechanical properties, dimensional stability, and deviations in tolerance we are prepared for using the Lithoz DLP printer for example/test components.

With high confidence, we can accurately manufacturer component to meet the needs of SNL.

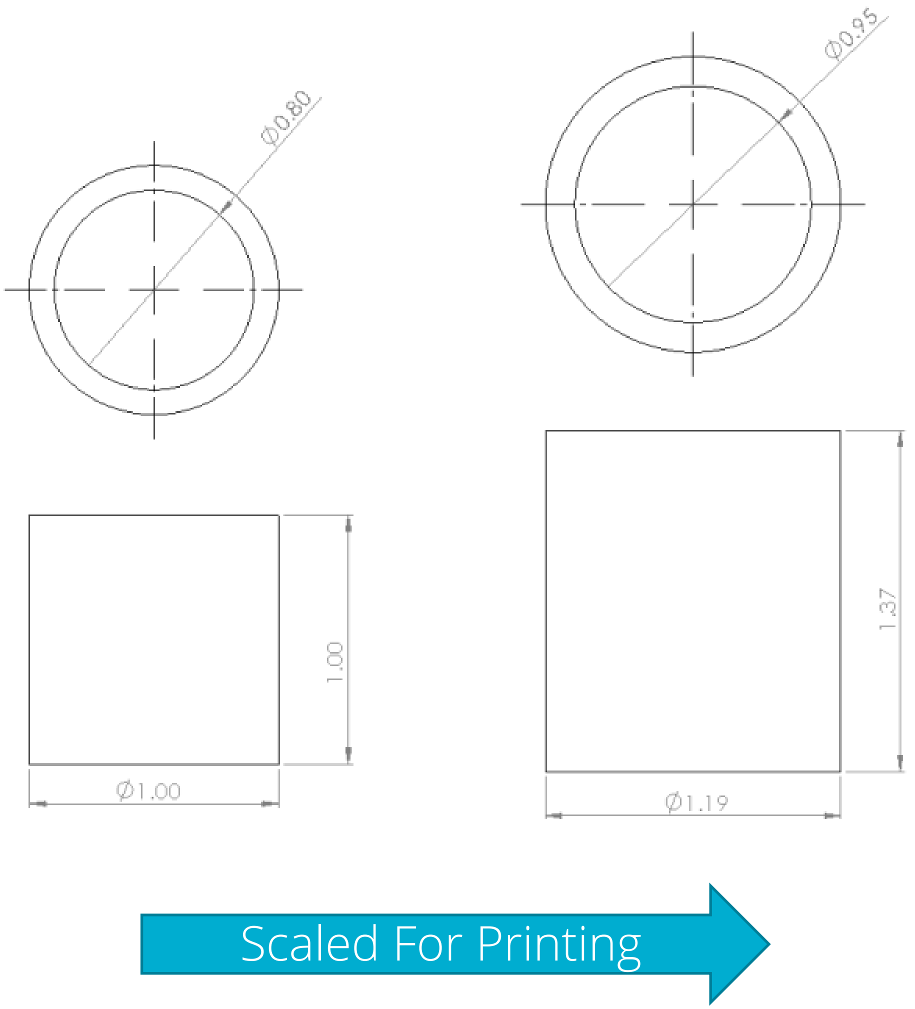


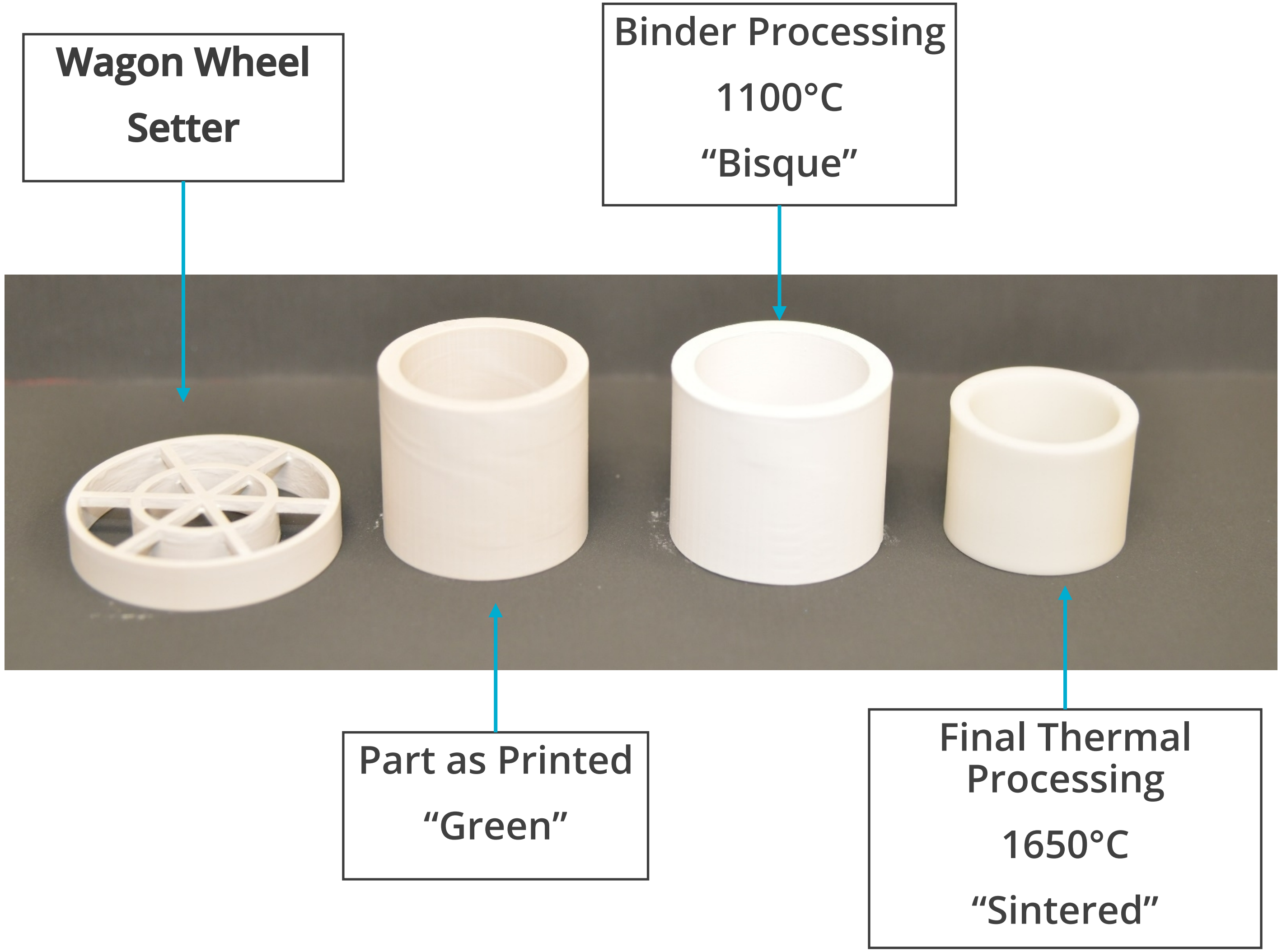


EXAMPLE COMPONENT

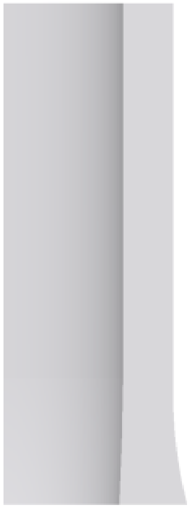


Preparation and Printing Components

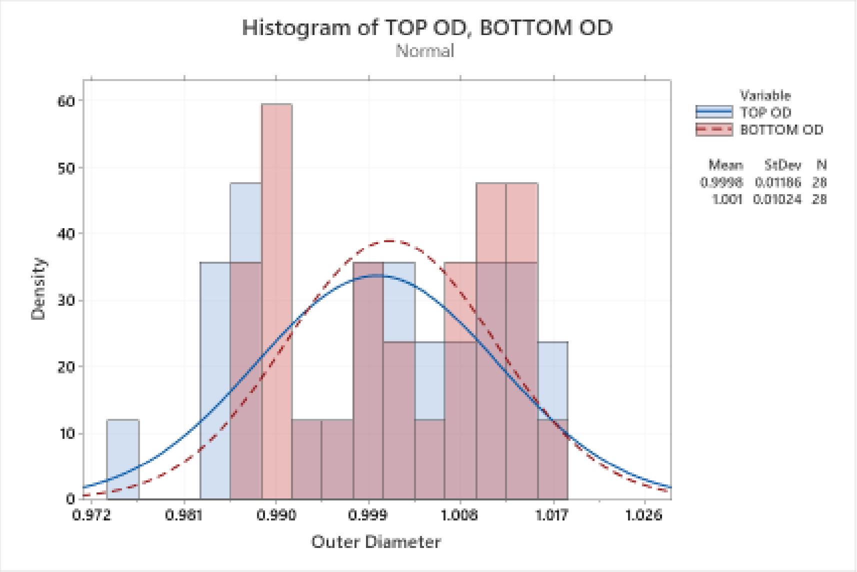


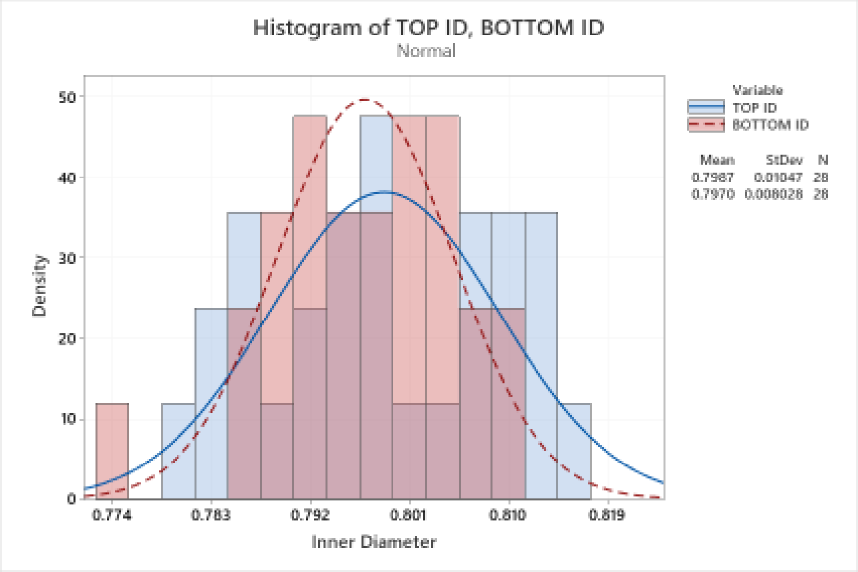


Error when printing and sintering



"Elephant Foot" and warpage observed post thermal processing.



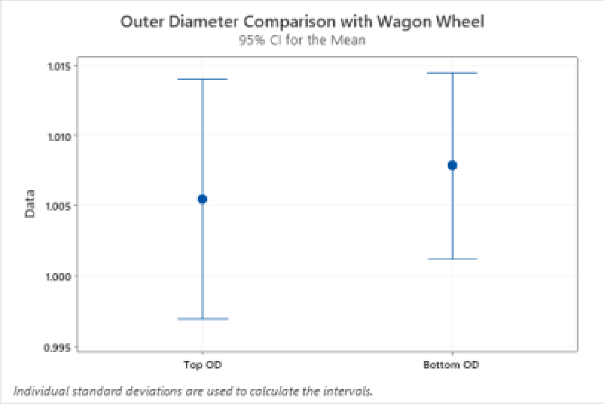


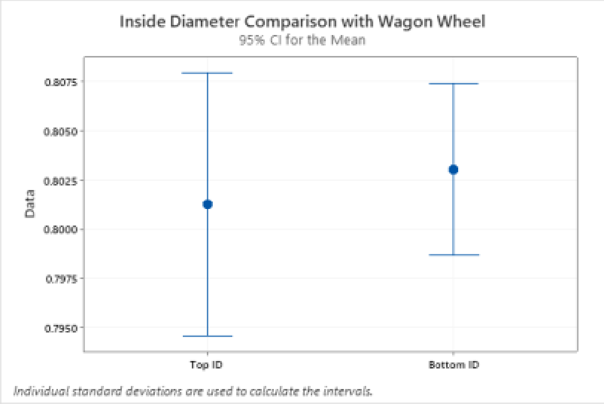
Design and Process Improvements to Address “Elephant Foot”

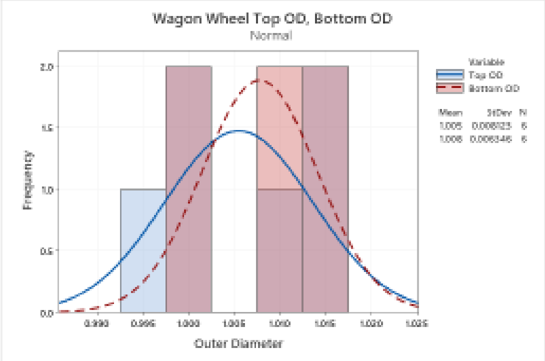
Initial attempt to address differences in Top vs. Bottom Dimensions.

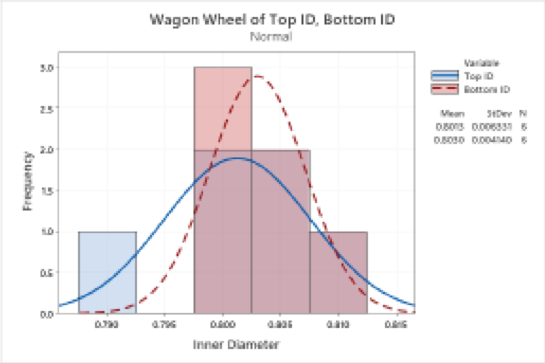
Sacrificial setter designed to allow contraction of the bottom of component at the same rate as the top.

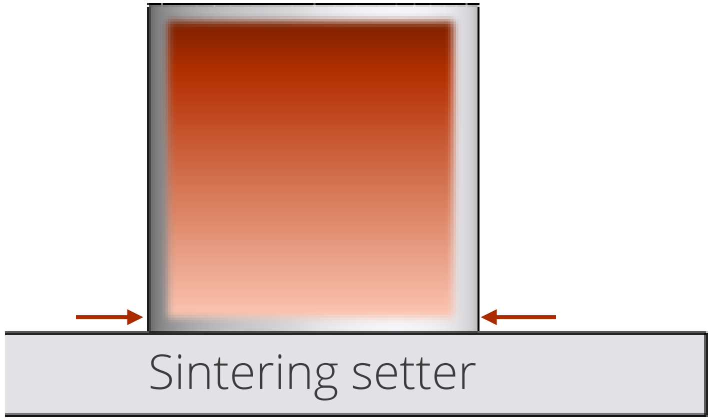
The sacrificial setter did not resolve the tolerance issues.

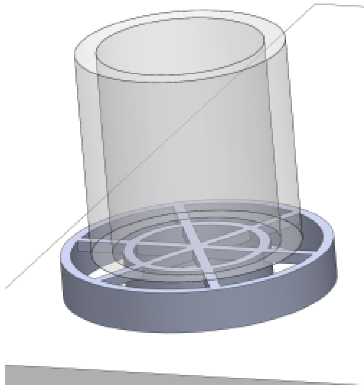






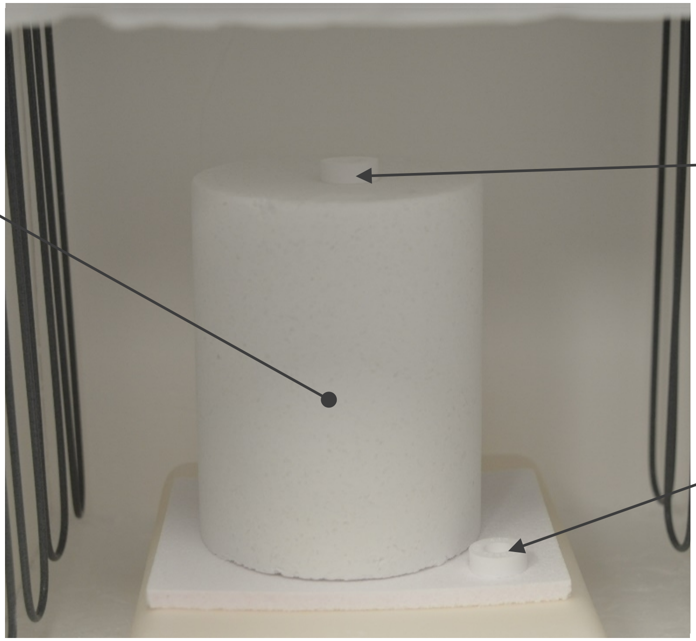


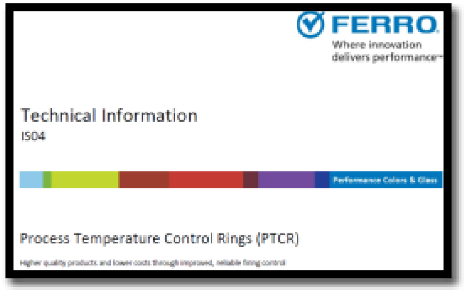




DOE of Ferro Thermal Rings

Thermal Measurement Data and Results				
Furnace Set Point	1550°C	1575°C	1600°C	1625°C
ΔL	1.86 mm	2.02 mm	2.22 mm	2.41
Corresponding Temperature (MAX)	1628°C	1645°C	1663°C	1695°C
Temperature Range	1610°C – 1628°C	1628°C – 1645°C	1658°C – 1663°C	1685°C – 1695°C
Tolerance of co-fired Test Samples (Average)	OD +0.005 ID -0.0015	OD +0.005 ID -0.005	OD +0.002 ID -0.003	OD +0.003 ID -0.003
Observations	Minimal sidewall/elephant foot	Both 1575°C and 1600°C Improved tolerance with not connection to setter		Slight bonding between setter and sample





FUTURE WORK ON CERAMIC INSULATOR

Based on results of the Ferro process temperature control rings, additional oven processing controls will be put in place. Experimentation is needed to calibrate controlling temperatures.

Conduct repeatability study for ceramic insulator with new process settings.

Repeat flexural bend test on 8 groups with improved thermal performance.

Continue to refine printing strategy to reduce manufacturing time and optimize thermal processing.

Develop initial framework for Qualification of Ceramic Additive Manufactured components, using Lessons learned from Metal Additive Manufacturing,

Developing a Conductive Ceramic Cermet

Lithoz America and SNL teamed together in 2021 to develop a printable Alumina/Molybdenum based Cermet.

We explored two options for this development.

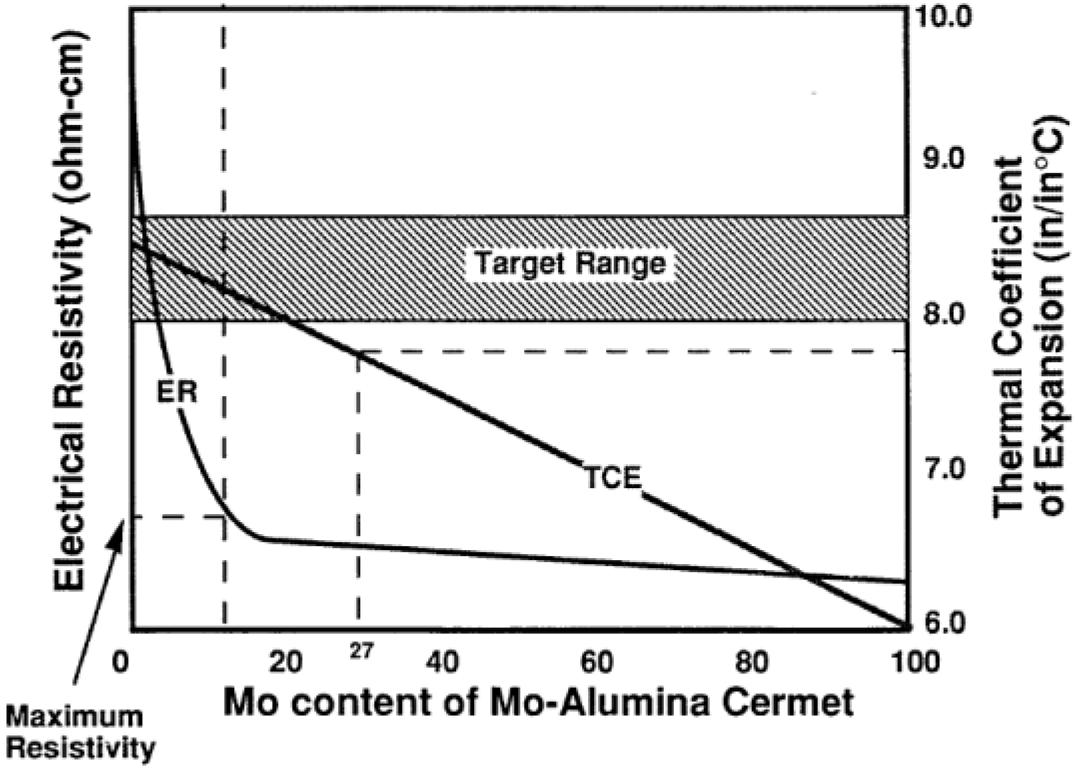
1. The first development used a pure Molybdenum powder combined with SNL's Alumina.

2. The second development uses Molybdenum Oxide combined with SNL's Alumina.

Challenges in Manufacturing Conductive Ceramics

Developing a co-fired cermet is a balance between Electrical Resistivity, Molybdenum Concentration, and Thermal Expansion Coefficient.

The design application requires the Cermet to provide an electrical connection while maintaining hermetic sealing capability.

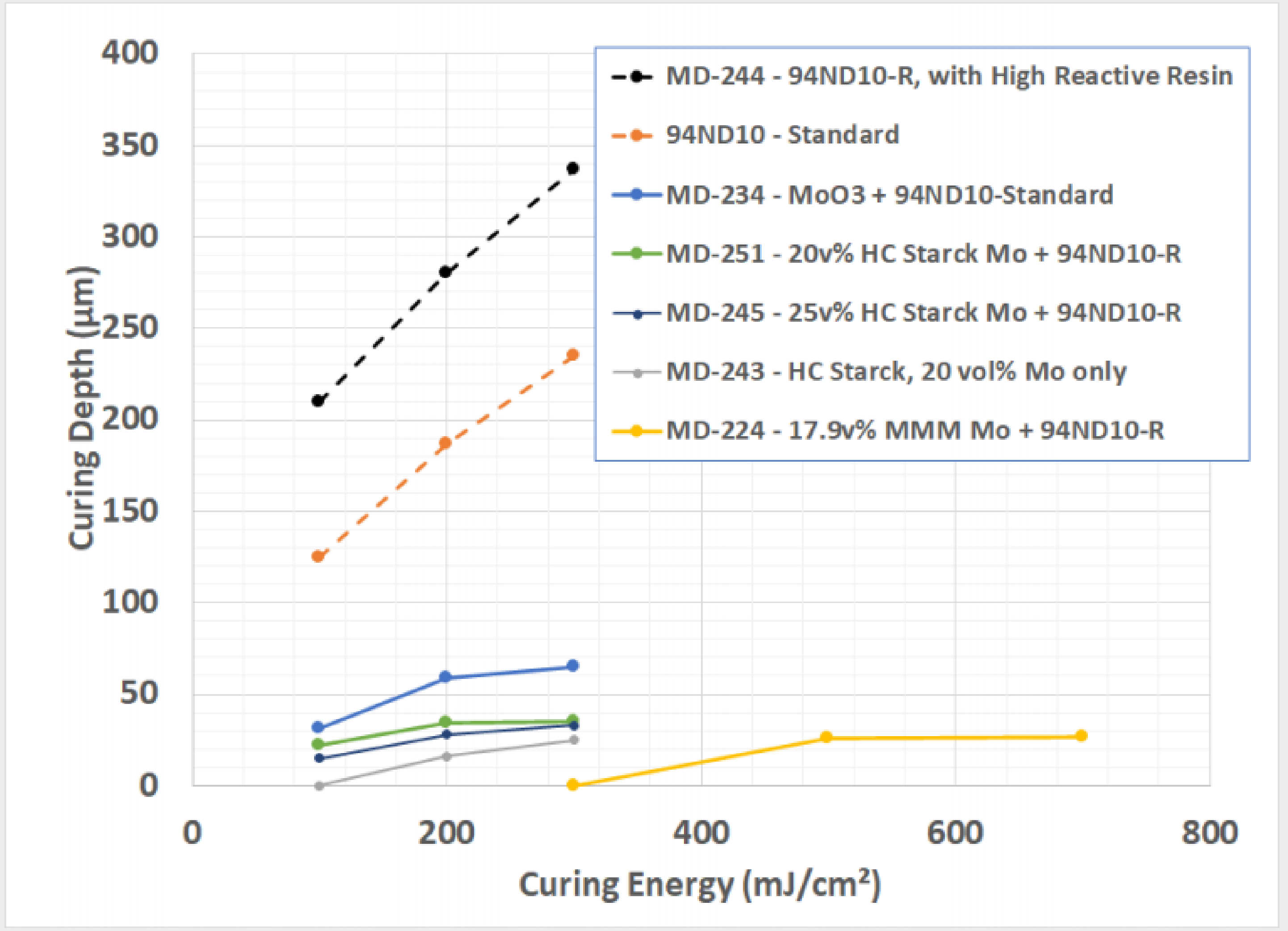


Pressley, G. (1996), Characterization of Molybdenum-Alumina Cermets [Masters Thesis, University of Florida]

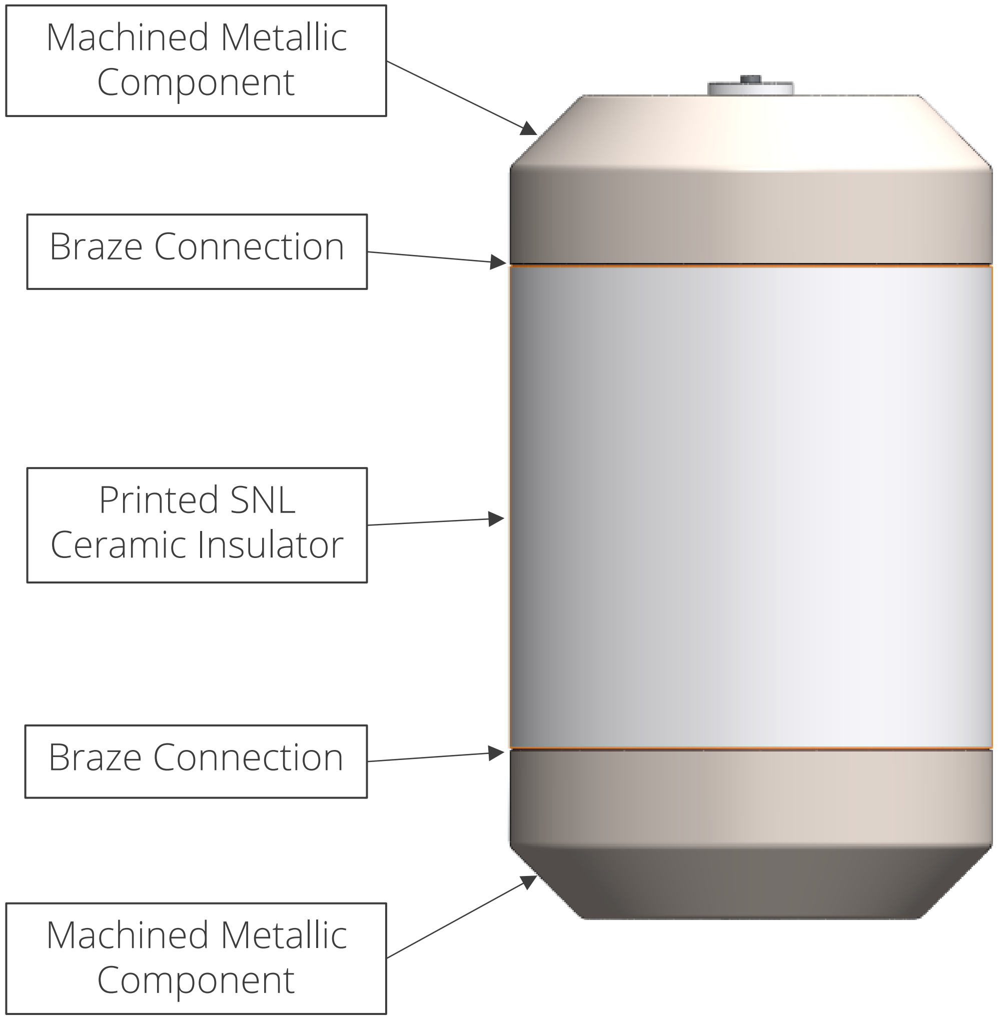
Curing Studies

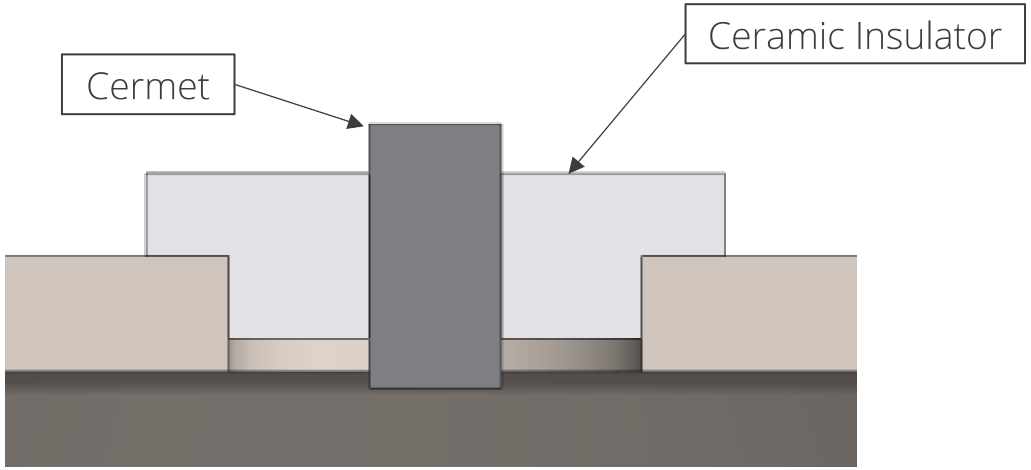
To test for manufacturability, a curing study was conducted by Lithoz America.

As expected, the molybdenum powder reduced the transparency of the material and resulted in less light penetration.



The Need of Multi-Material Ceramics





THE SUCCESS OF ATTENDING AMUG IN 2021

- In 2021, SNL set out to develop a Alumina and Molybdenum conductive ceramic cermet.
- The available SNL Molybdenum did not meet the needs of to transform into a printable slurry.

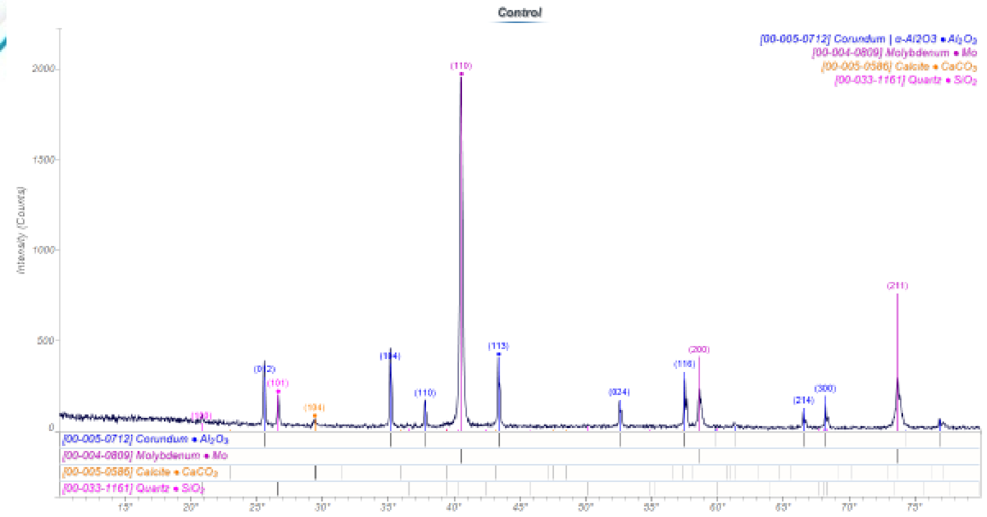
H.C. Starck Moly Powder size		
		Range
D50	4.6 µm	3.5 – 5.5
D99	18.99 µm	20 max

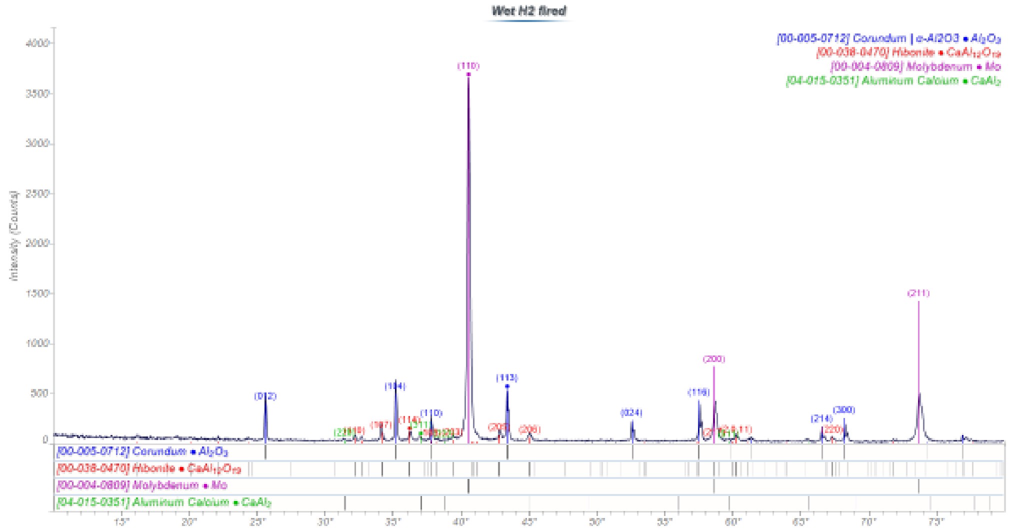
H.C.Starck

High Performance Metal Solutions

SNL Moly Powder size	
D10	6 µm
D50	10 µm
D90	28 µm

Manufacturing and Testing with H.C. Starck Powder

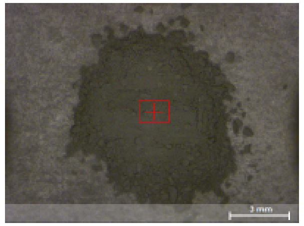


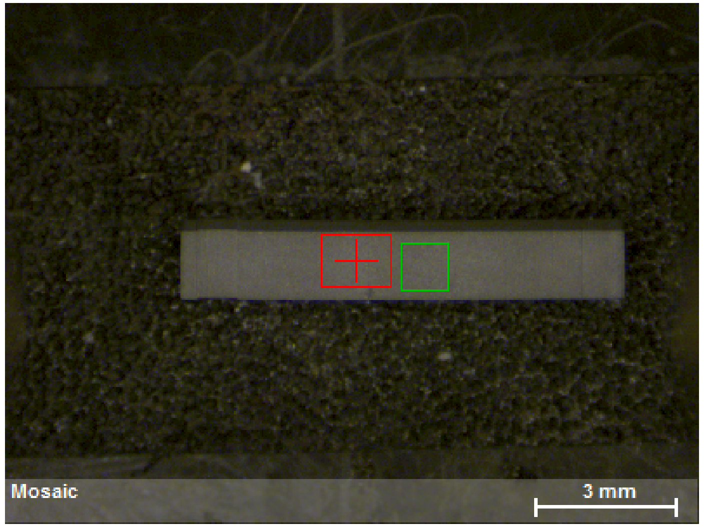


Spectrum: PostFire.txt

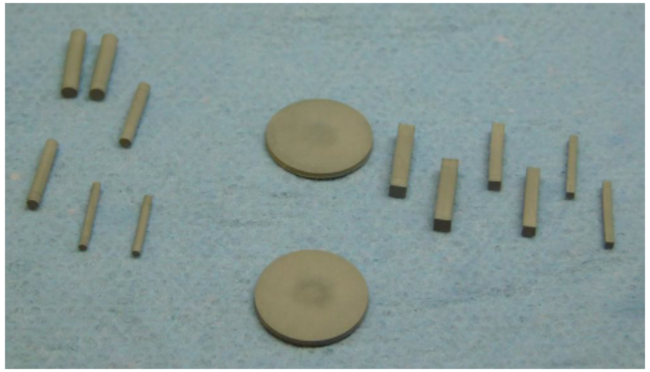
El	AN	Series	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
W	74	L-series	0.24	0.06	0.00
Mo	42	K-series	60.22	30.29	0.16
Ca	20	K-series	1.49	1.79	0.00
Al	13	K-series	37.81	67.62	0.38
Ti	22	K-series	0.08	0.08	0.00
Cr	24	K-series	0.07	0.07	0.00
Co	27	K-series	0.06	0.05	0.00
Fe	26	K-series	0.03	0.02	0.00
Rh	45	K-series	0.00	0.00	0.00
		Total:	100.00	100.00	

Scan Area (10x):





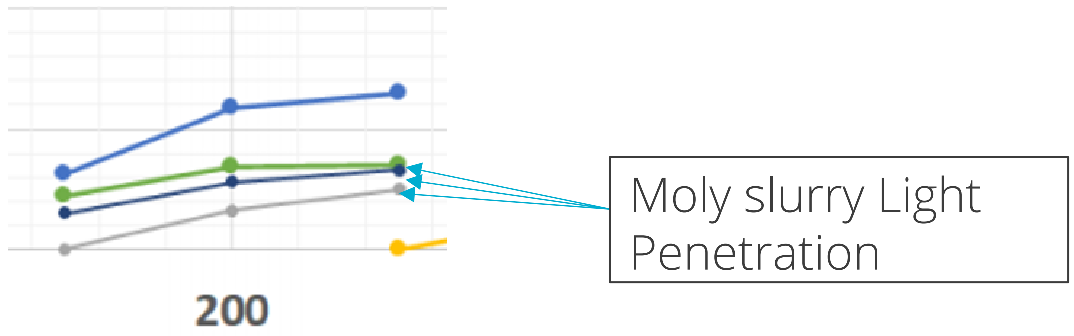
Printed Alumina and 99.95% Mo Samples

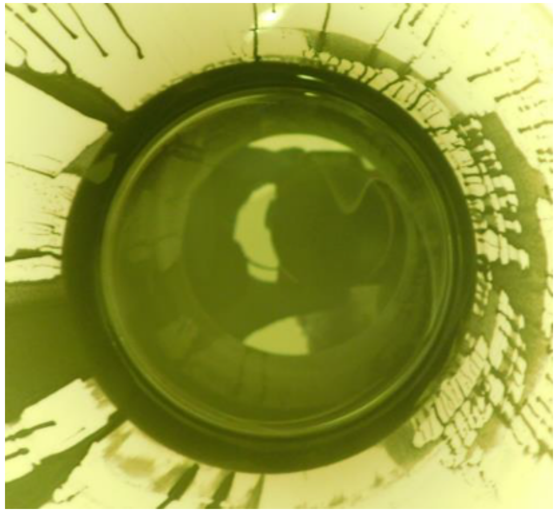


Pure Molybdenum Cermet Summary

+ During thermal processing, Mo volume remains relatively constant.
+ Increase moly content with adjustments to particle size.
+ Initial attempts with H.C. Starck powder was successful.
+ 20 volume % in final mixture

- Formation of oxide during binder removal is a risk
- Overall printability with decreased layer thickness
- Settling of molybdenum during storage



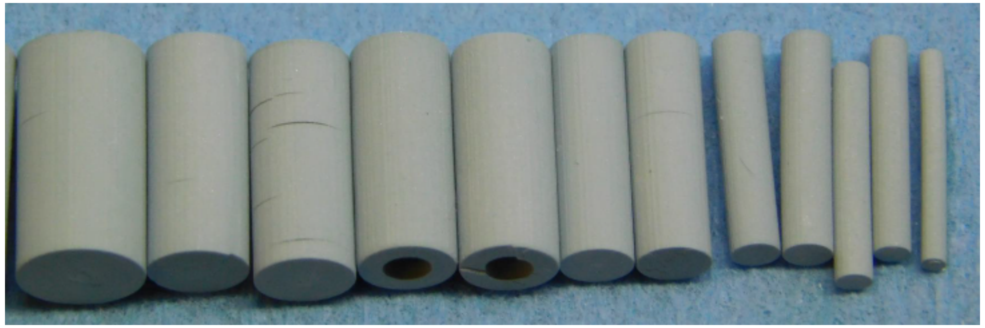


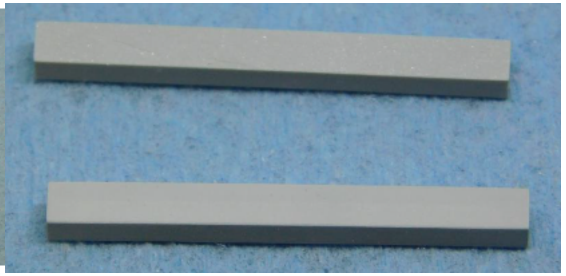
Developing the MoO_3 Cermet

Identified and sourced 6μm MoO_3 powder.

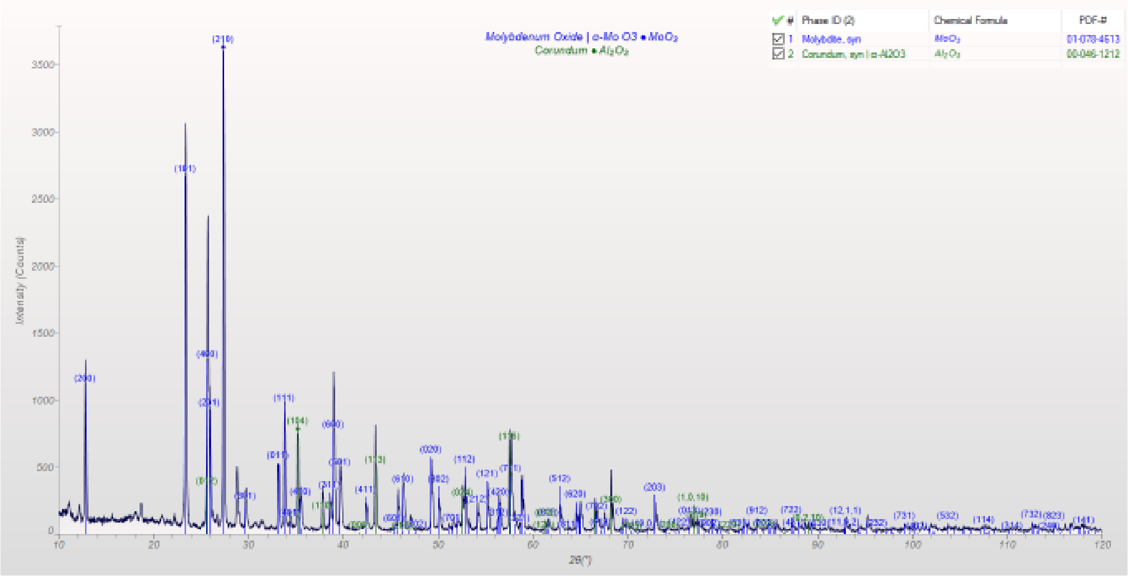
Blend with SNL's 94% alumina powder and Lithoz resin

Once combined, reduction of the MoO_3 will take place in a Hydrogen environment.

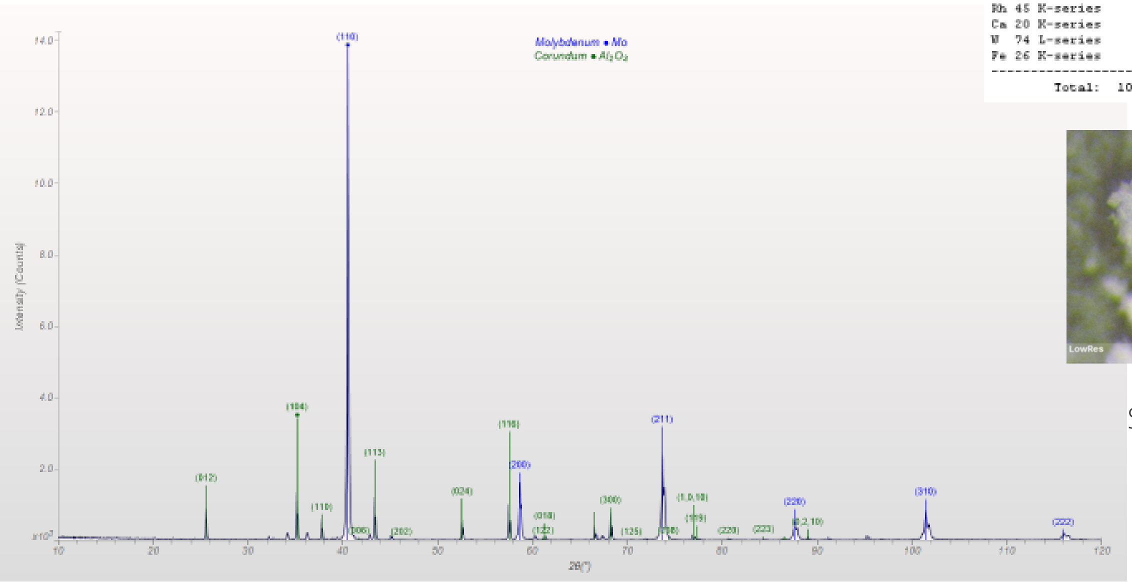




Pre-Fired Scan

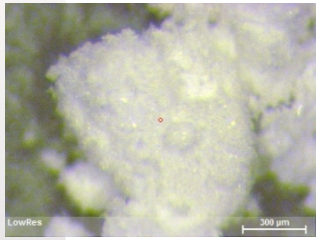


Post-Fired Scan



Spectrum: prefire.txt

El	AN	Series	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
Mo	42	K-series	71.43	41.58	0.17
Al	13	K-series	27.64	57.21	0.16
Rh	45	K-series	0.00	0.00	0.00
Ca	20	K-series	0.83	1.16	0.00
W	74	L-series	0.07	0.02	0.00
Fe	26	K-series	0.03	0.03	0.00
		Total:	100.00	100.00	



Scan Area (10x):

Molybdenum Oxide Cermet Summary

+ With the use of MoO_3 we can increase the Mo content in the final product.
+ Material is fairly stable through the de-binding process.
+ Ease of milling for particle size adjustment.
+ Superior light penetration to pure molybdenum
+ 25 volume % in final mixture
+ Increased stability during storage

- Balance between removing oxide and sintering for full density.
- Can introduce instability during reduction of the Molybdenum Oxide

SNL Selected to Mature the MoO_3 Cermet

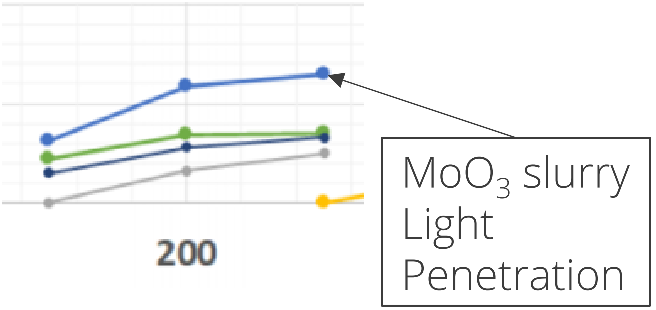
Lithoz America manufactured test quantities of the MoO3/Alumina slurry for SNL evaluation and maturation.

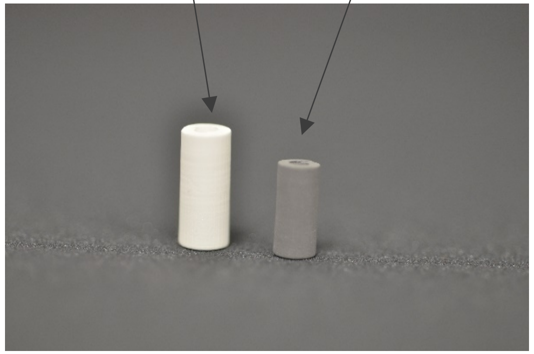
The SNL Lithoz printer is a single material machine. Manufacturing of the components was conducted separately and combined following the printing process.

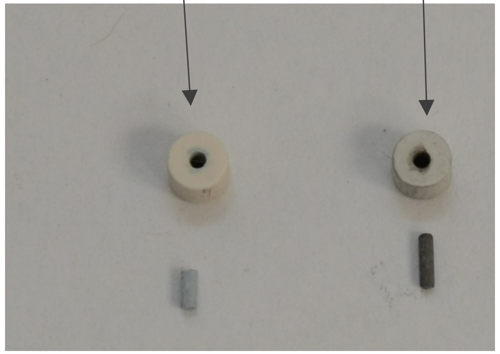
SNL manufactured components for characterization:

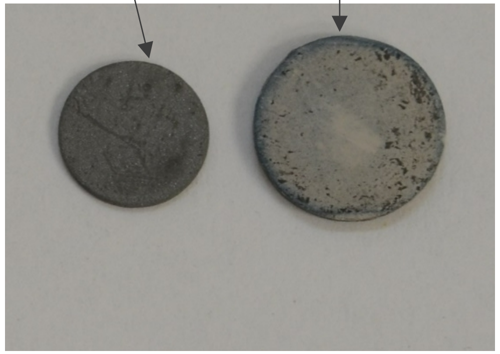
The desired feed-thru shown on in the example component requires a cermet diameter of 0.040” inserted

MoO_3 and Alumina Slurry





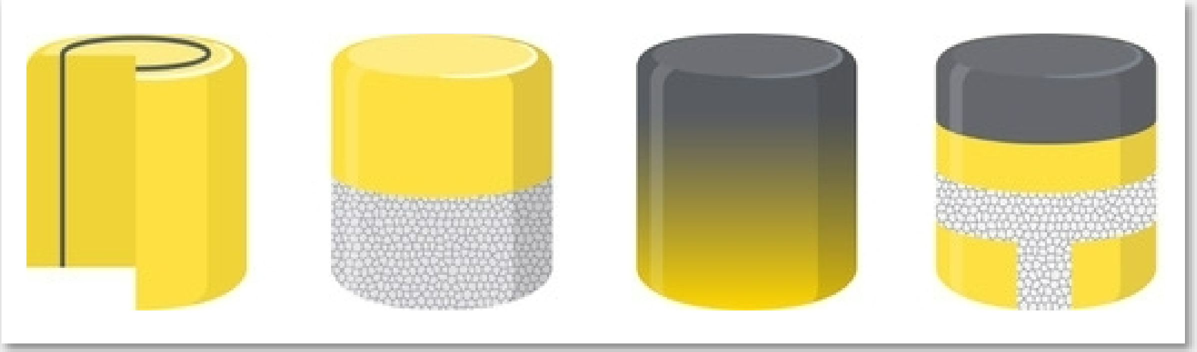




Multimaterial DLP Printer

LITHOZ

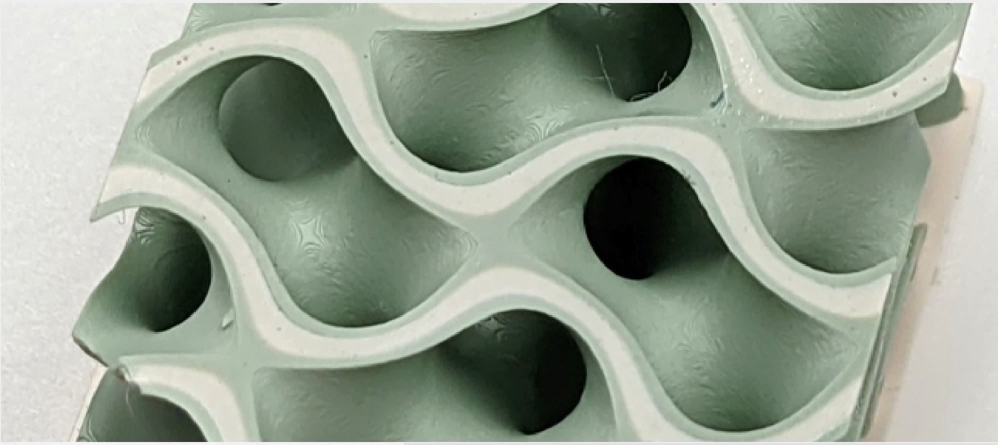
- Two moveable vats with one build platform
- Cleaning step between material changes to prevent cross contamination



Multi-Functional Properties

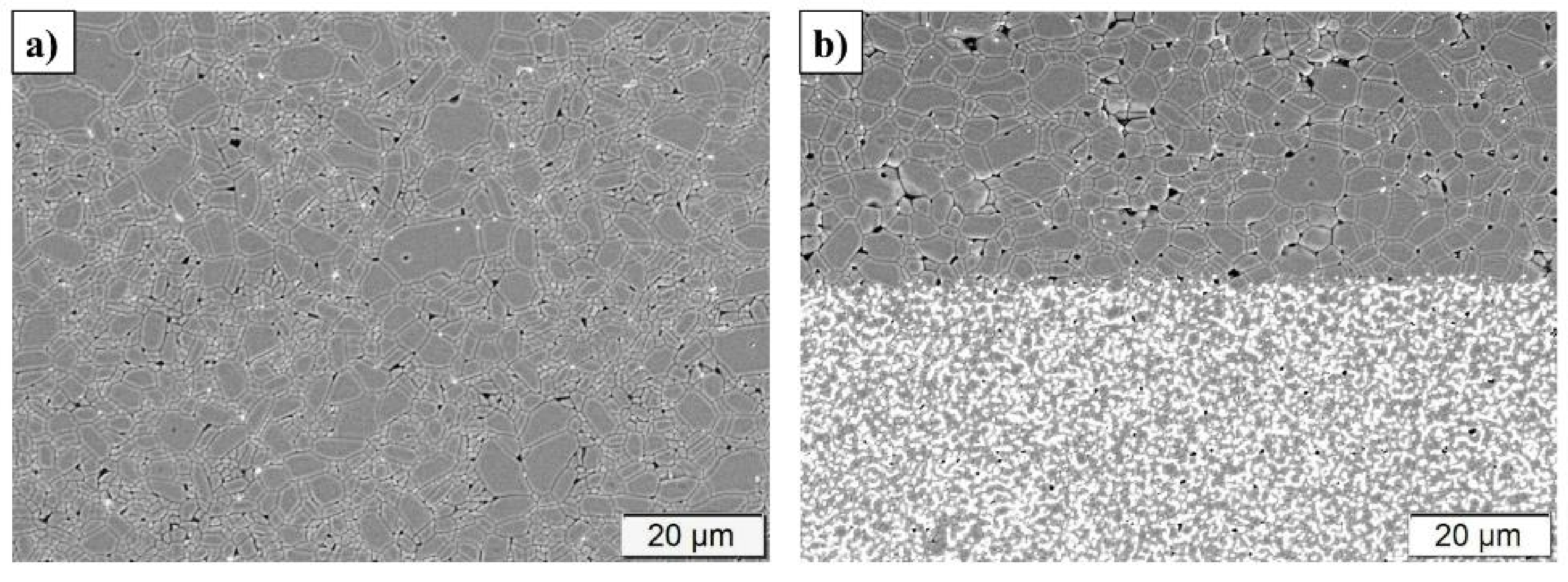
Combine different properties in one component

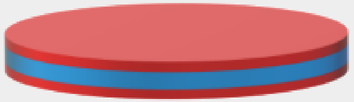
- Porous | dense
- Bioresorbable | bioinert
- Electrically conductive | insulating
- Magnetic | non-magnetic
- Hard | ductile
- Heat conductive | heat insulating
- Transparent | opaque
- Color



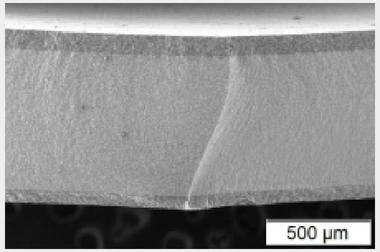
Superior Strength by Design

A





A-ZTA-A



- Synergistic strength improvement achieved than for ZTA or Alumina alone → similar to tempered glass
- Homogeneous microstructure
    - A-region: Average 2 µm grains of alumina with broad distribution
    - ZTA-region: Average 1 µm grains for alumina and zirconia, narrow distribution
- Sharp interface between A and ZTA regions

Schlacher, J., et al (2021). Additive manufacturing of high-strength alumina through a multi-material approach. *Open Ceramics*, 100082.

Multi-Material 3D Printing - Outlook

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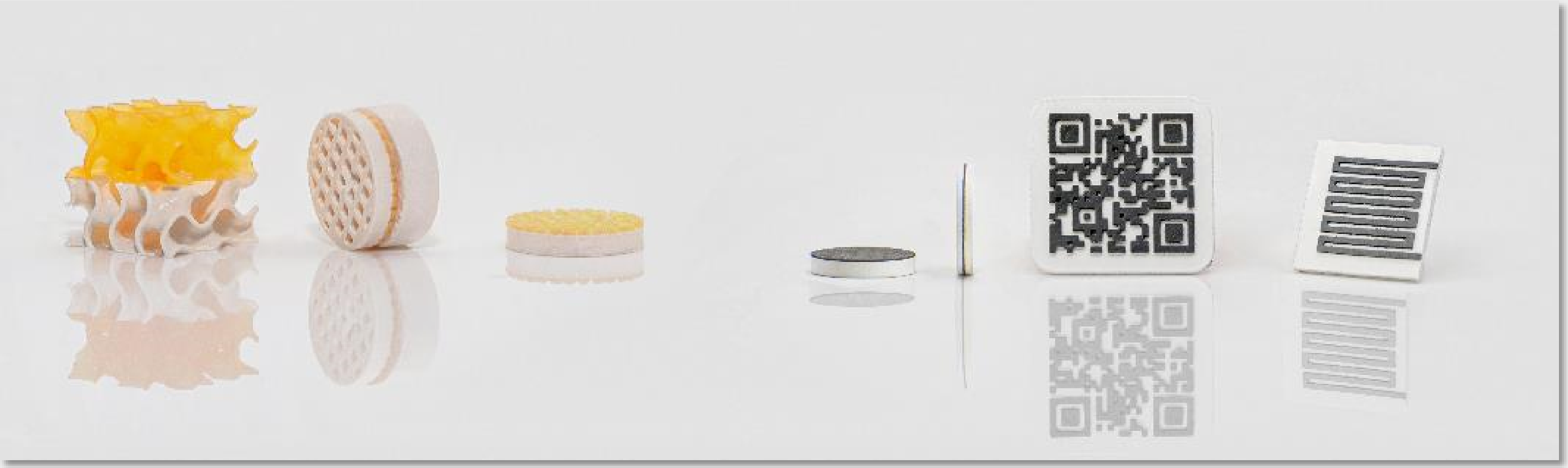
Going beyond purely ceramic systems

ceramic - polymer | ceramic - metal



Alumina | Polymer

Zirconia | Stainless steel
Green Parts

Combining Ceramic and Metal

2022 Projects Initiated

SNL and Lithoz America continue teaming in 2022, with new material developments.

Three materials to develop in 2022:

1. ZnO ceramic for Varistor development
2. Alternate 94% SNL alumina
3. Next Generation Cermet enabling bond between insulator and cermet.

Conclusion

Through successful teaming with Lithoz America, we have develop, matured, and tested various ceramic components in multiple different products.

Ceramic Additive manufacturing at SNL is growing and was recently awarded significant dedicated effort that will start in 2023!

Continued refinement to SNL's 94% alumina will improve the performance and make non-traditional manufactured components available.

SNL's need for multi-material aligns well with the future efforts of Lithoz!

By continued investments from our stakeholders, ceramic additive manufacturing is enabling our designers to push the limits for next generation products.

Thank You!

Sandia National Laboratories

LITHOZ®

Manufacture the future.

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