Cryomilled 17-4 Stainless Steel Powder as Feedstock for Additive Manufacturing

Frank Kellogg,[1] Andelle Kudzal,[2] Clara Mock,[3]
Josh Taggart-Scarff,[1] Ryan Rogers,[4] and Brandon McWilliams[2]

[1]SURVICE Engineering Company, Belcamp, MD 21017
[2]CCDC Army Research Laboratory (ARL), APG, MD 21005
[3]ORAU, Belcamp, MD 21017
[4]Bowhead Science and Technology, Belcamp, MD 21017

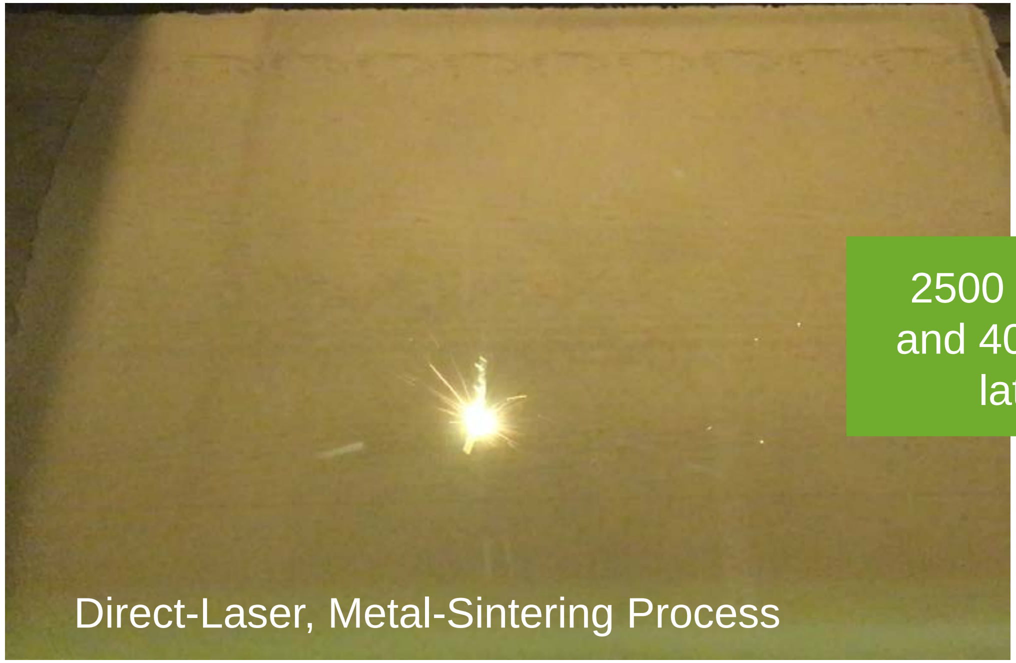
U.S. ARMY

DEVCOM ARMY RESEARCH LABORATORY

DSIAC Defense Systems Information Analysis Center

Additive Manufacturing (AM)

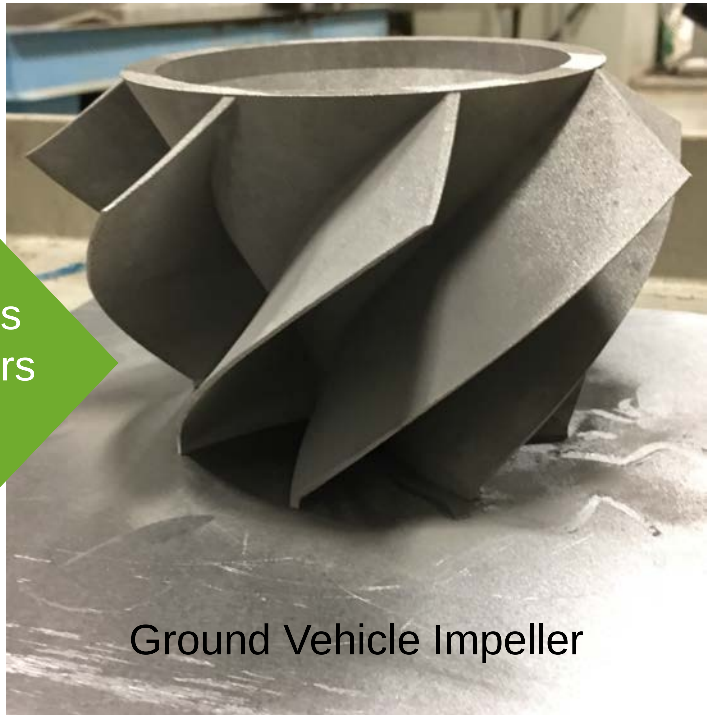
Additive manufacturing is the process of joining materials to make objects from 3-D model data, usually ***layer upon layer***, as opposed to subtractive manufacturing methodologies (such as machining).



Direct-Laser, Metal-Sintering Process

Click to View Video

2500 layers and 40 hours later

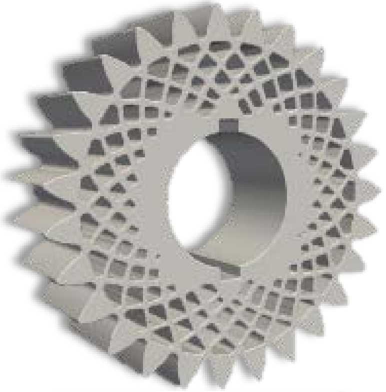


Ground Vehicle Impeller

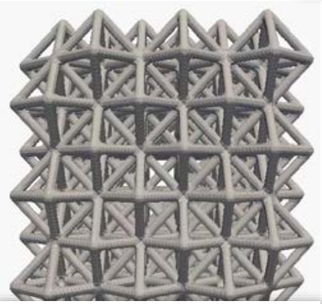
Army challenge: Deliver *quantified* parts to the Warfighter to support mission readiness and increase performance through advanced materials and designs.

Benefits of AM for the Army

- **On-Demand Manufacturing at the Point of Need:**
  - Reduce inventories
  - Reduce logistics tail
  - Mission readiness and adaptability
- **Complexity**
  - Easier/cheaper to implement
  - Designs not possible through subtractive methods
- **Expedite Design Process**
- **Rapid Materials Development**

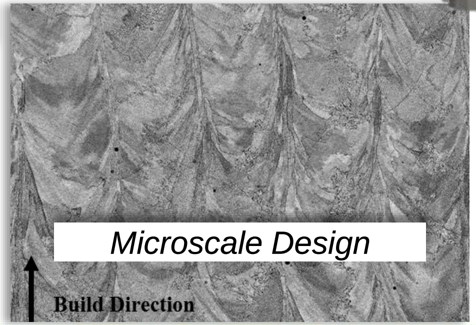


Macro Design



Mesoscale Design

Customized Gear



Microscale Design

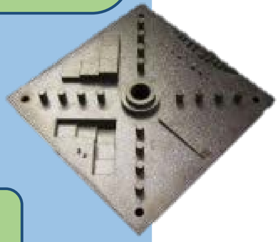
ARL Direct Metal Laser Sintering Scope

Manufacturing

Powder Bed
Powder Fed
Novel

Metals AM

Benchmarking



NIST Test Artifact

Post-Processing (HT, HIP, Machining, Surface Finish)

Qualification and Certification

Materials/Feedstock Development

Optimized Alloy Design
Computational Thermodynamics

Powder Production
Cryomilling and Atomization

Characterization

In-situ Sensing and Control

Laser

Feedstock

AM Components
- Mechanical Properties
- Porosity/Defects, Residual Stresses, and Distortions/Geometry

Processing/Microstructure/Property Relations

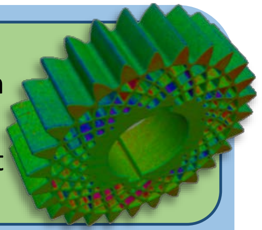
MATERIALS AND MANUFACTURING SCIENCE
AM Research

EXPEDIENT MANUFACTURING
In-Theater Capabilities

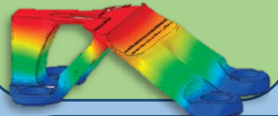
APPLICATIONS
High-Performance Structural Components

Modeling and Simulation

Design Tools
- Topology Optimization
- CAD
- Physics-Based Support Structures



Performance
- FEA
- Microstructure-Based Prediction of Mechanical Properties



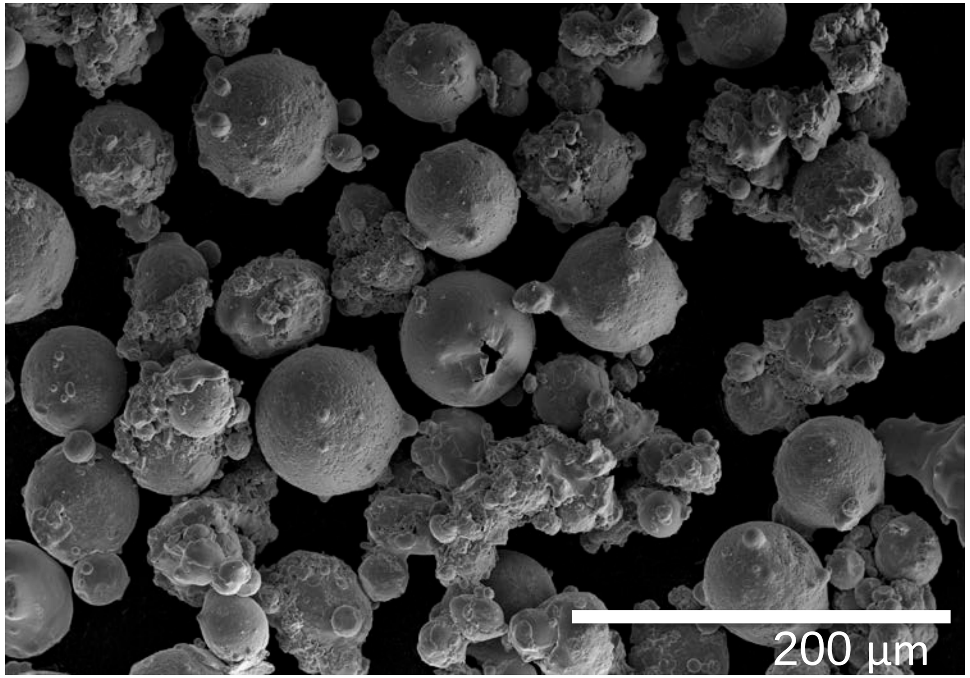
3-D Scanning and CAD Generation

Process Models
- Microscale (Powder/Melt Pool)
  - Solidification, Thermodynamics, Phase Field, Microstructure Prediction, and Evolution
- Continuum
  - Process Modeling, Thermal Histories, Residual Stresses, Distortion, Microstructure-Based Prediction of Mechanical Properties

AM Powder

- **AM powders are not always “pretty.”**
  – Defects in the powder can influence build behavior.
  – Powder porosity does not easily go away.

- **Powder processing can be applied to AM powders to improve build properties.**
  – Remove powder porosity.
  – Change powder morphology.
  – Nanostructuring.



Ball Milling in Liquid Cryogen

- Relatively low energy
- Cryogen prevents oxidation
- Produces nanostructured, micrometer-sized particles
- Strength and processing stability
- Surface chemistry modifications
- Morphology manipulation

Cryomilling

Brand New Mill Design

- Powder can be introduced to mill after loading in glove box.
- Powder is discharged as a slurry with cryogen and can be moved directly into glove box antechamber.
  - Controlled atmosphere/cryogen can boil off to mitigate exposure to air.
  - Powder can be worked with inside glove box.

Mixing Propeller With Laser Sensor for Determining/Controlling Height of Cryogenic Slurry

Cryomilling: AM - Motivations

Cons
Morphology Changes Loss of sphericity
Contamination Media/vessel debris
Melt-Based Processing AM process dependent
Extra Steps = Extra Costs Cryomilling and degassing

Pros
Surface Chemistry Changes
Flowability Cryomilled Al powder flows much easier than Al powder
Alloy Design Mechanical alloying
Improved Properties Mechanical properties and conductivity

Processing: Cryomilling and Degassing

- **Cryomilling Processing Parameters**
  - 2-kg 17-4 stainless steel powder atomized in Ar
  - 0.15 weight% steric acid
    - Process control agent to avoid excess cold welding
  - 32:1 media to powder weight ratio
    - ¼” diameter 440C stainless steel
  - 2 hours of cryomilling

- **Degassing**
  - Fluidized powder degasser w/inert atmosphere
  - Removes steric acid
  - Parameters determined via TGA

Processing: AM Parameters

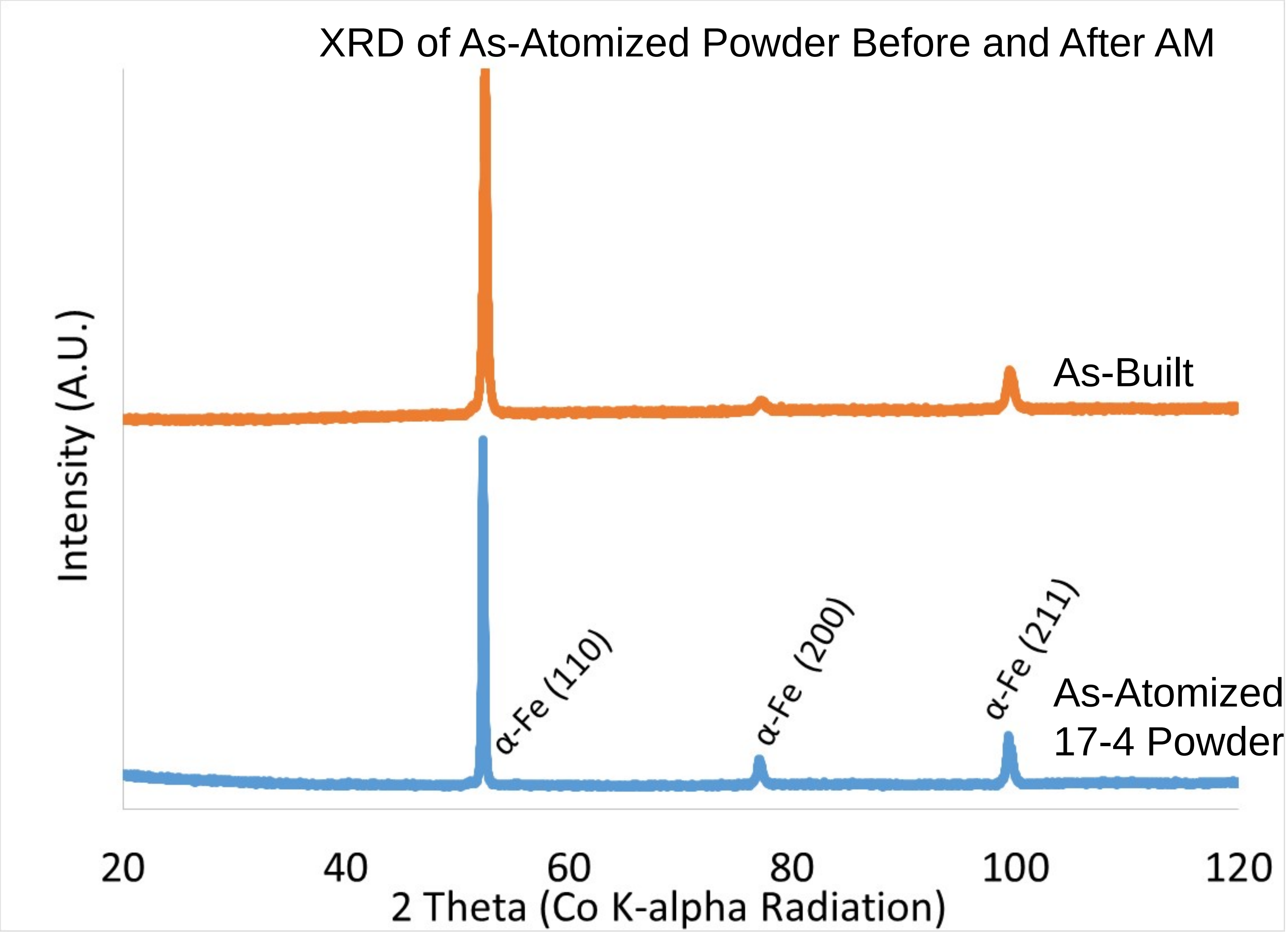
- Laser Power: 49 W
- Laser Scan Speed: 140 mm/s
- Hatch Spacing: 0.07 mm
- Powder Layer Thickness: 0.03 mm

Parameters chosen based on previous 17-4 production

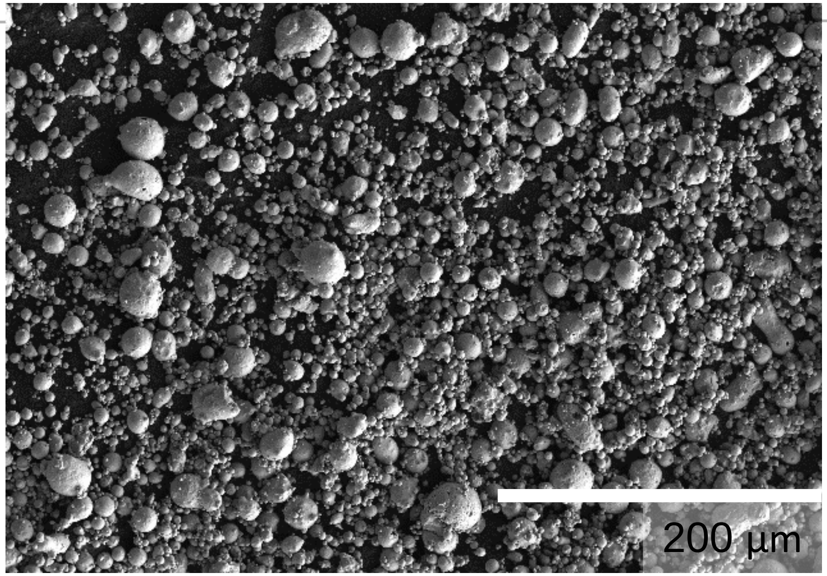
PROX DMP 100

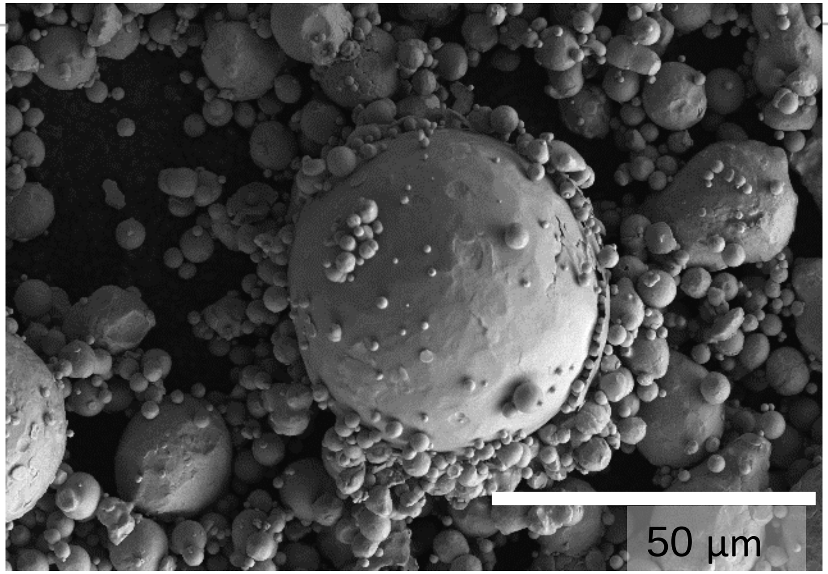
Image from 3dsystems.com

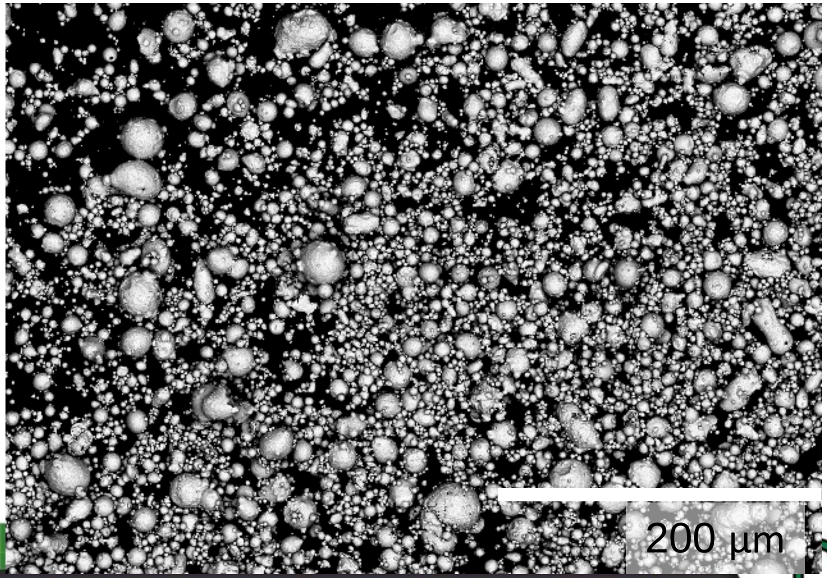
Powder Characterization: Pre-Cryomilling

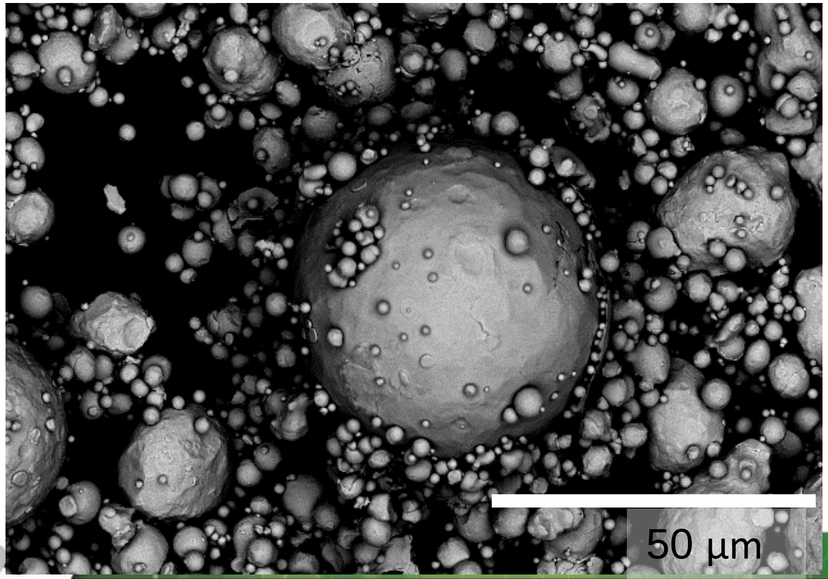


Powder Characterization: Pre-Cryomilling





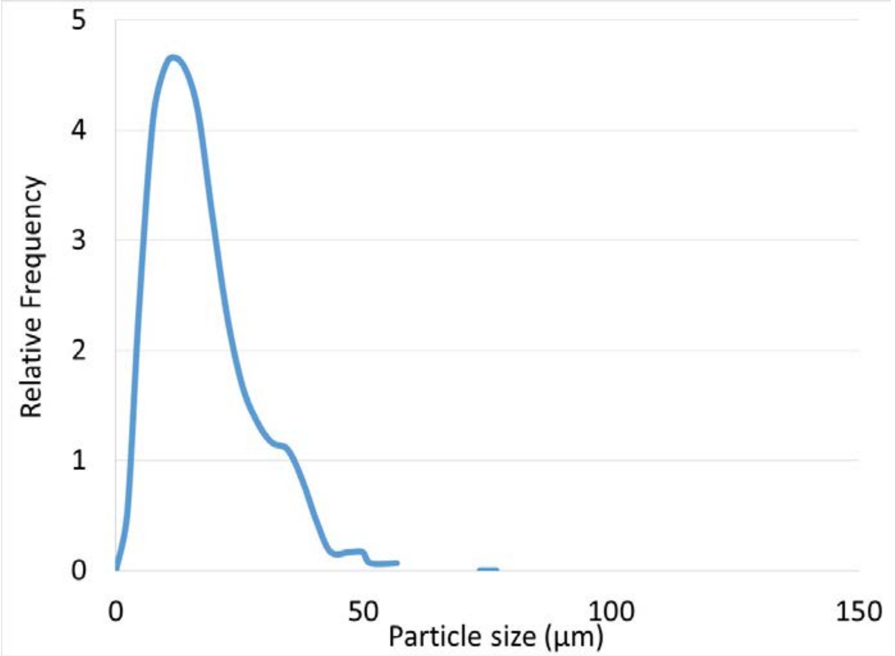




Powder Characterization: Pre-Cryomilling

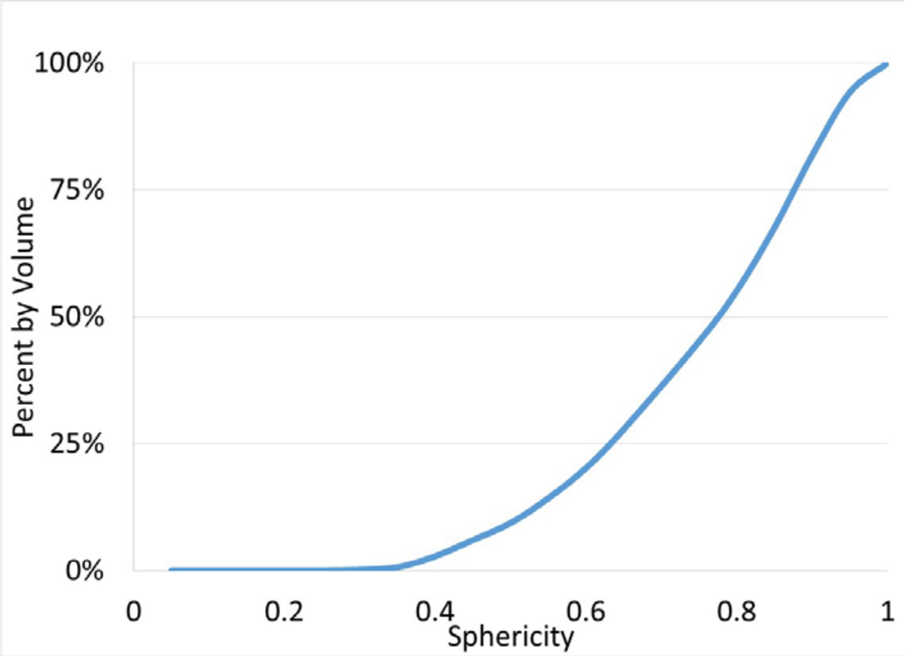
As-Atomized Powder Particle Size Distribution and Shape Analysis

- Measured via dynamic image analysis with Retsch Camsizer X2
- Powder purchased as a -325 mesh cut



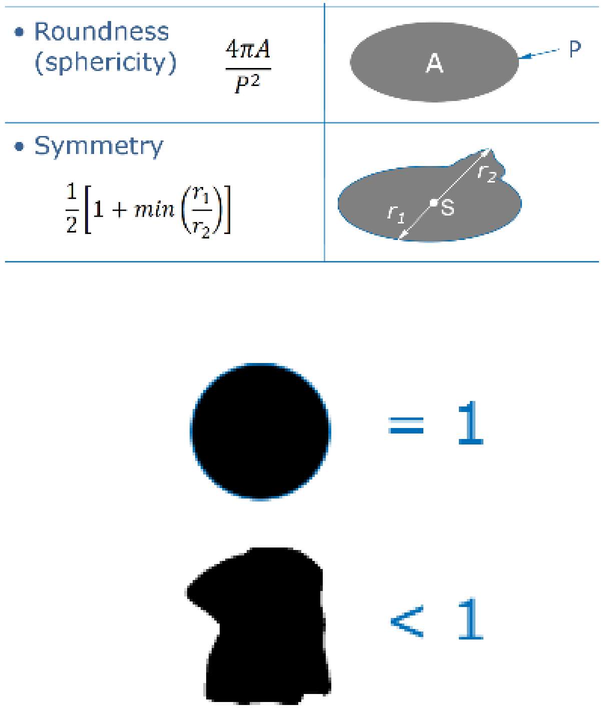
Particle Size Distribution (µm)

D10	6.38
D50	15.27
D90	32.16



Particle Morphology

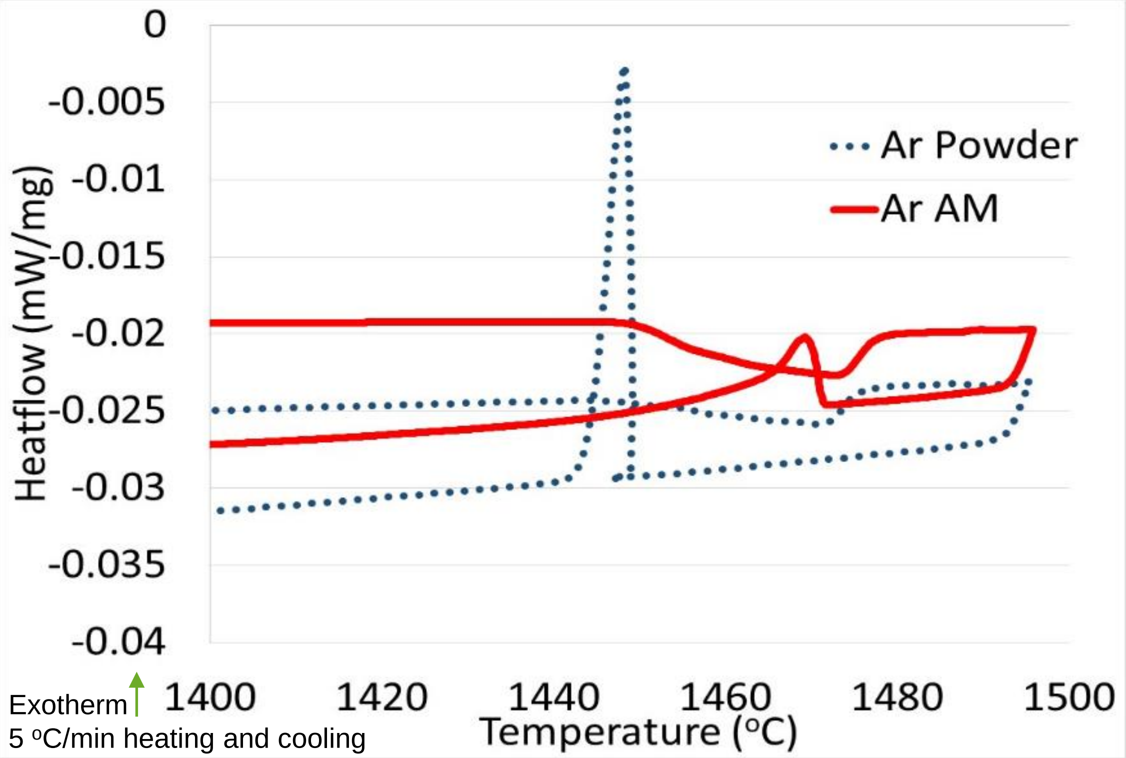
Mean Average Sphericity	0.74
Mean Average Symmetry	0.91



Figures provided by Retsch

DSC of As-Atomized Powder

- Ar-atomized 17-4 powder and as-manufactured AM 17-4 have same melting on set and completion points but different solidification points.
- Cause of peak shift not clear but may be from sample prep.



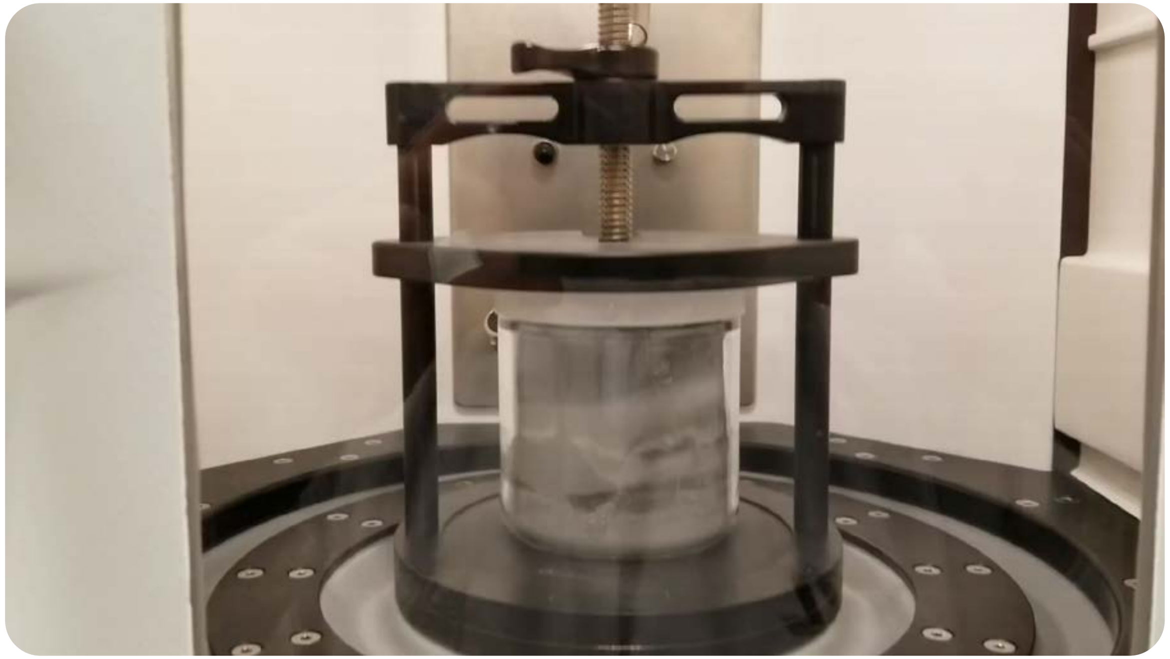
Powder Melting: 1448-1473 °C
As-Built Melting: 1450-1478 °C
Literature*: 1404-1440 °C
Powder Solidification: 1450 °C
AM Solidification: 1472 °C

*Specification Sheet: Alloy 17-4PH
https://www.sandmeyersteel.com/images/17-4ph-spec-sheet.pdf

Cryomilling: Process

Powder Preparation

- 2 kg, as-atomized in Ar, 17-4 SS mixed with 0.15 weight% stearic acid
- Acoustic mixing at 10-g acceleration for 1 hour in 1-kg batches
- Previous research: 24 hours in V-blender



Click to View Video

Two Cryomill Runs

1st run: coating run, powder not used for these experiments

- Improve yields of subsequent runs
- Decrease contamination of subsequent runs
- Yield: 1046 g, 52% yield

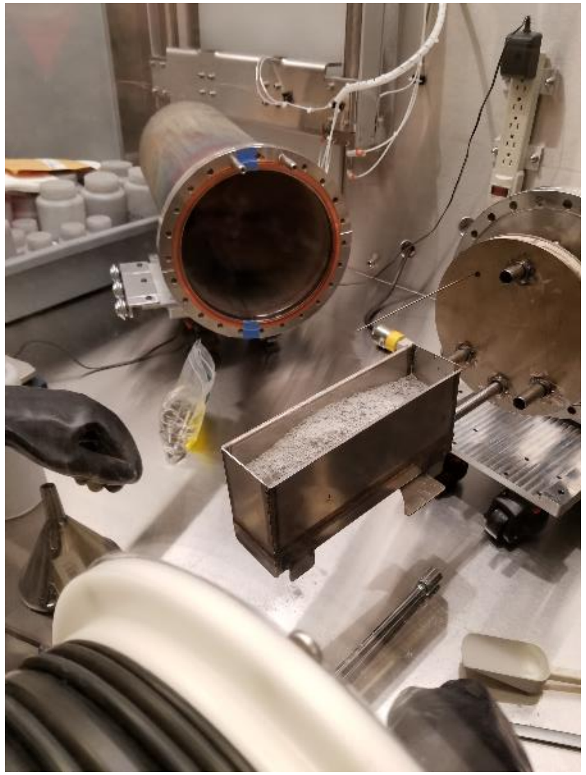
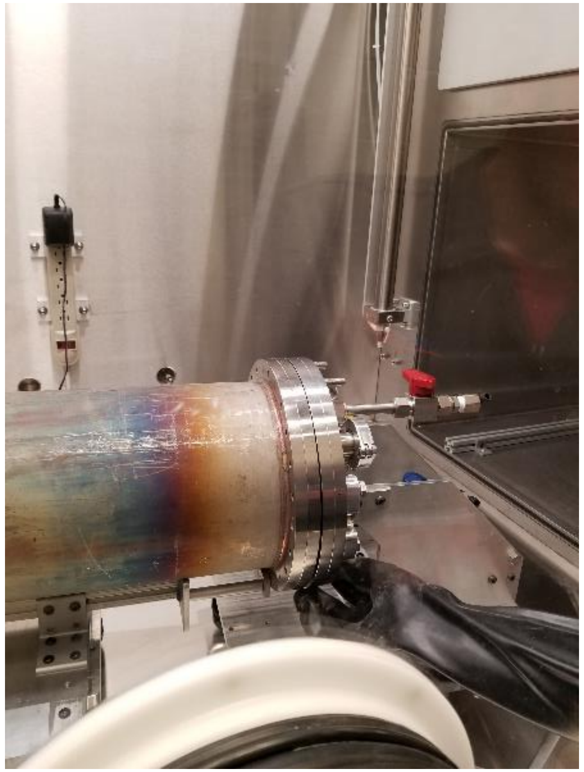
2nd run yield: 1411 g, 71% yield

- After degassing and sieving (-325 mesh): 823 g
  - 823 g “ready to use”: overall yield of 41%
    - 59% of degassed powder
    - +325: 542 g, 39% degassed powder, 27% overall

Degassing

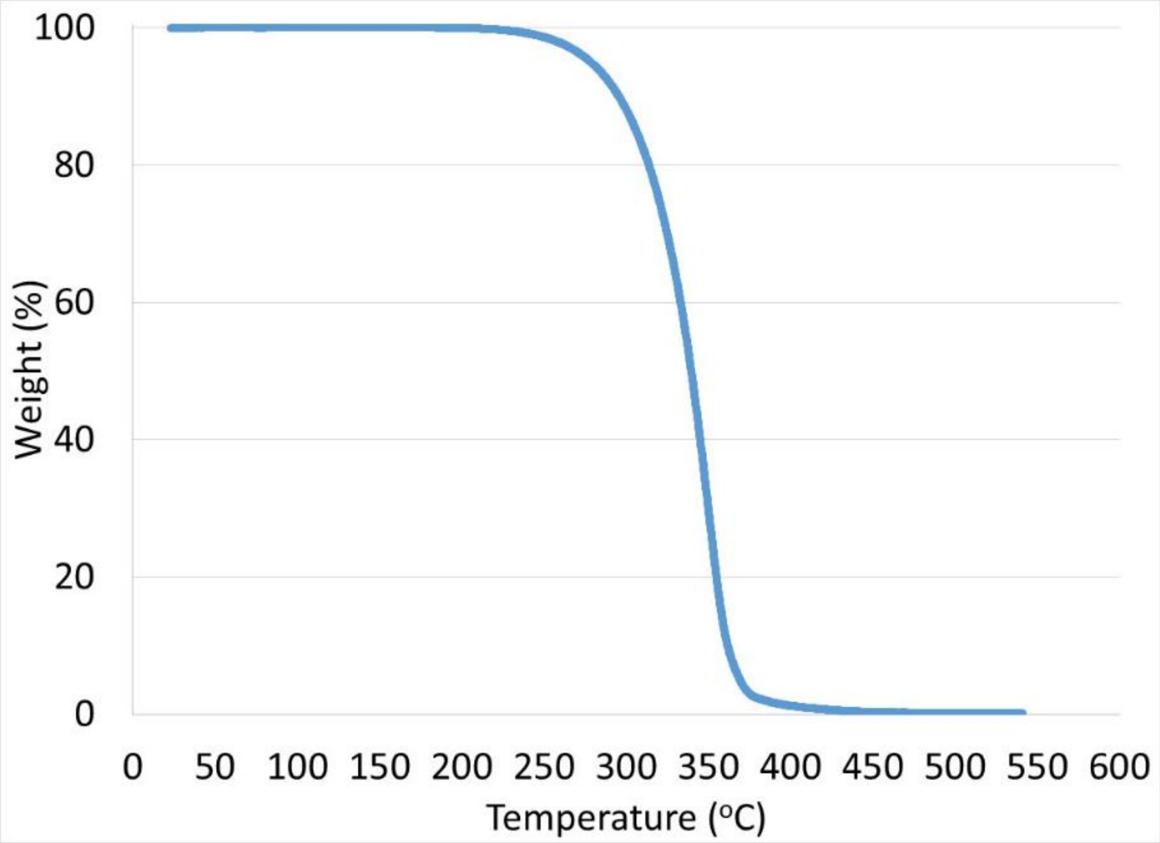
Removes Stearic Acid

- Fluidized rocking furnace with powder under flowing Ar
- Powder loaded and sealed in glove box under Ar

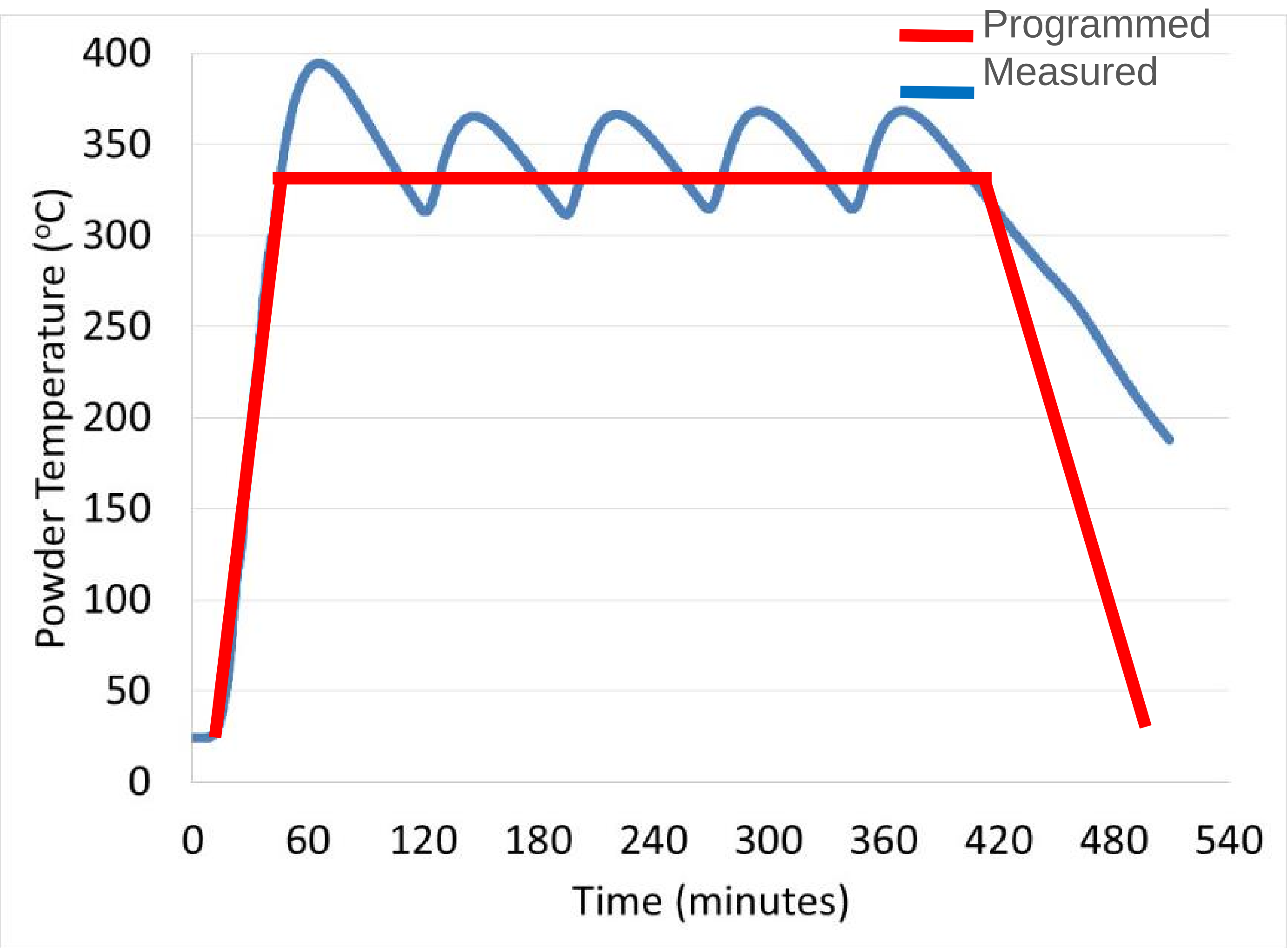

TGA of Stearic Acid

- Led to 325 °C for 6 hours, degassing schedule
- Needs high enough temperature and long enough durations to remove stearic acid but without changing microstructure



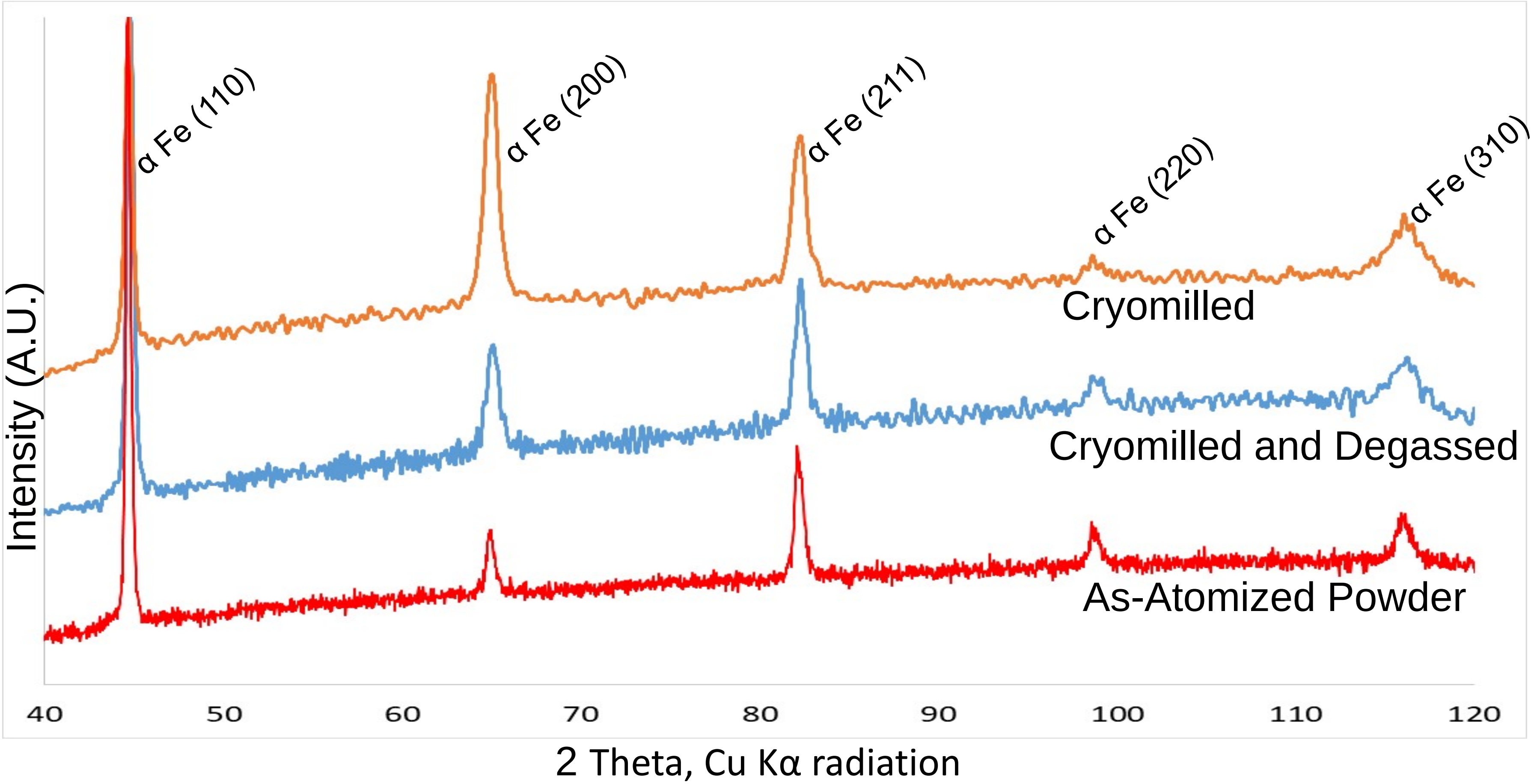
Degassing

- 10 °C/min to 325 °C, with a 6-hour hold
- 1st true run with furnace
  - PID issues



Cryomilled Powder: XRD Analysis

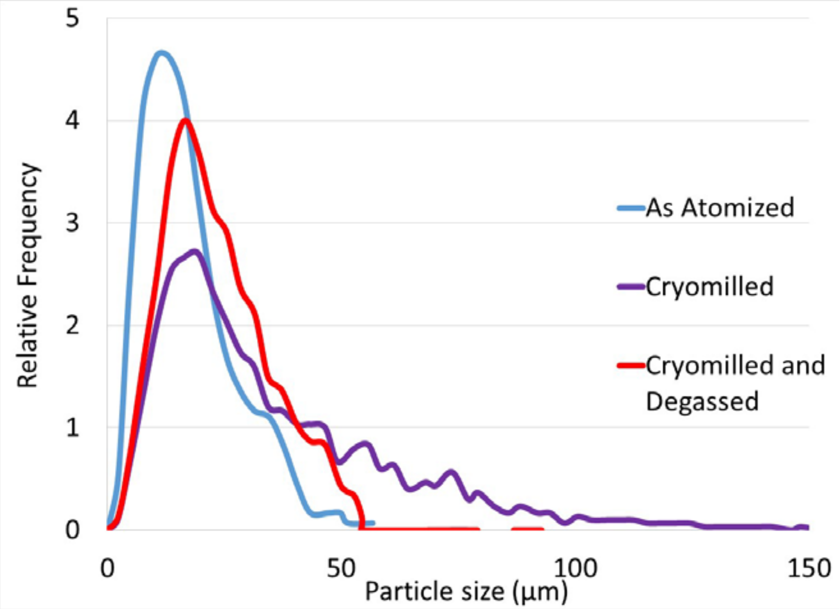
The cryomilling and degassing procedures did not lead to any phase changes.



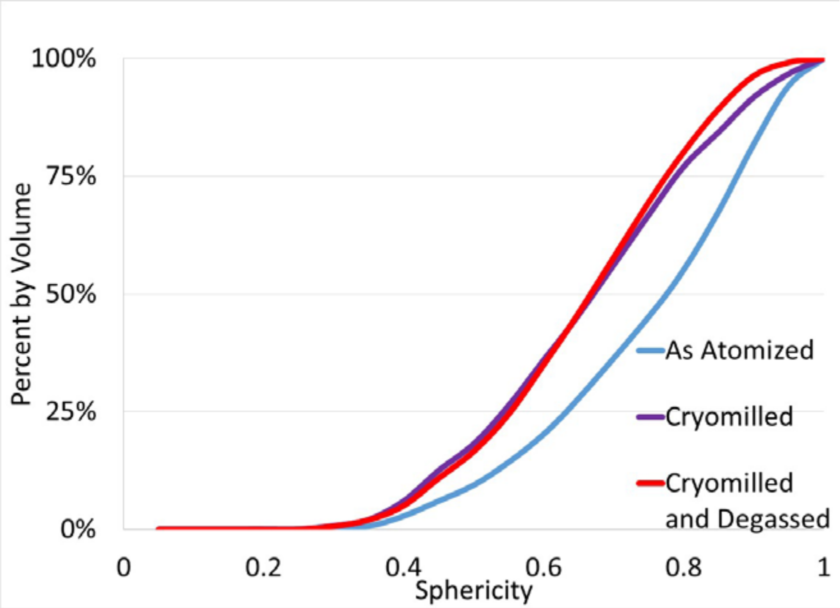
Cryomilled Powder: Particle Size Distribution and Morphology

Particle Size Distribution and Morphology Comparison of As-atomized, Cryomilled, and Degassed Powders

- Cryomilled powder was unsieved; degassed powder was hand-sieved with -325 mesh



Particle Size Distribution (µm)



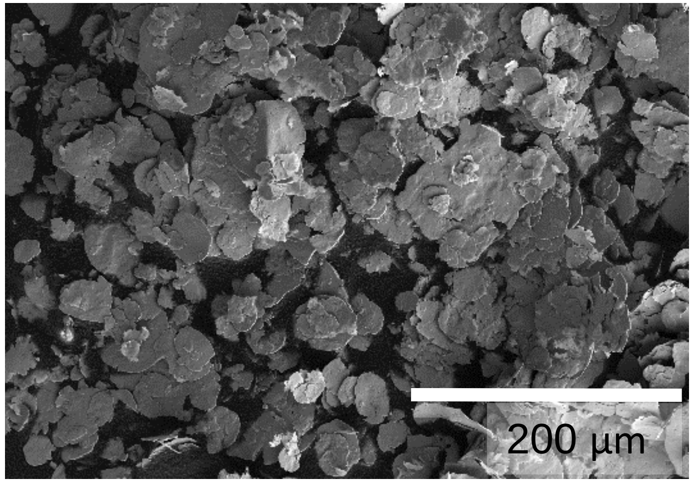
Particle Morphology

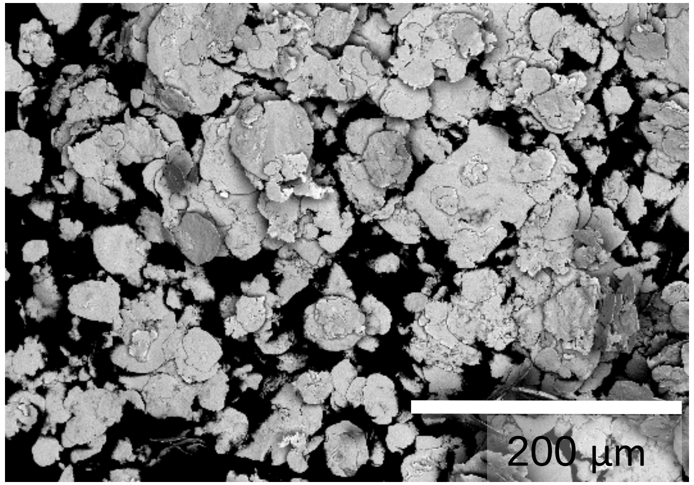
	As-Atomized	Cryomilled	Cryomilled and Degassed
D10	6.38	10.98	10.13
D50	15.27	27.50	21.41
D90	32.16	72.22	40.19

	As-Atomized	Cryomilled	Cryomilled and Degassed
Mean Average Sphericity	0.74	0.66	0.66
Mean Average Symmetry	0.91	0.89	0.89

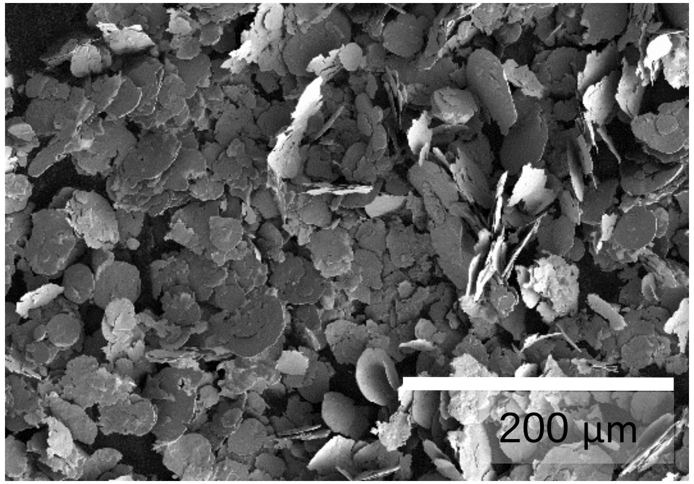
Cryomilled Powder: SEM

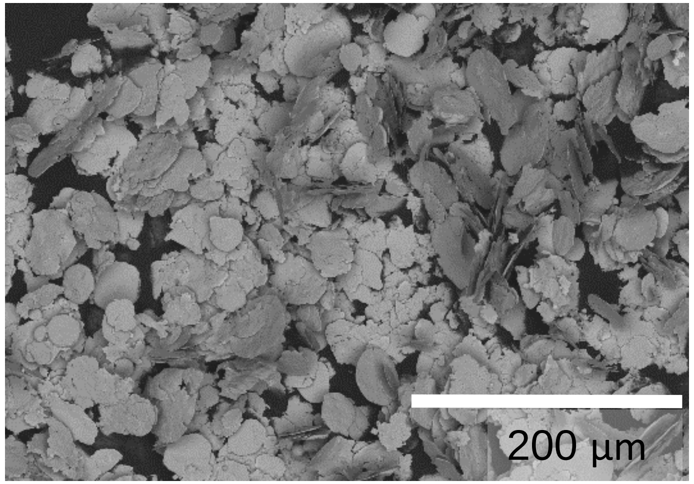
Cryomilled





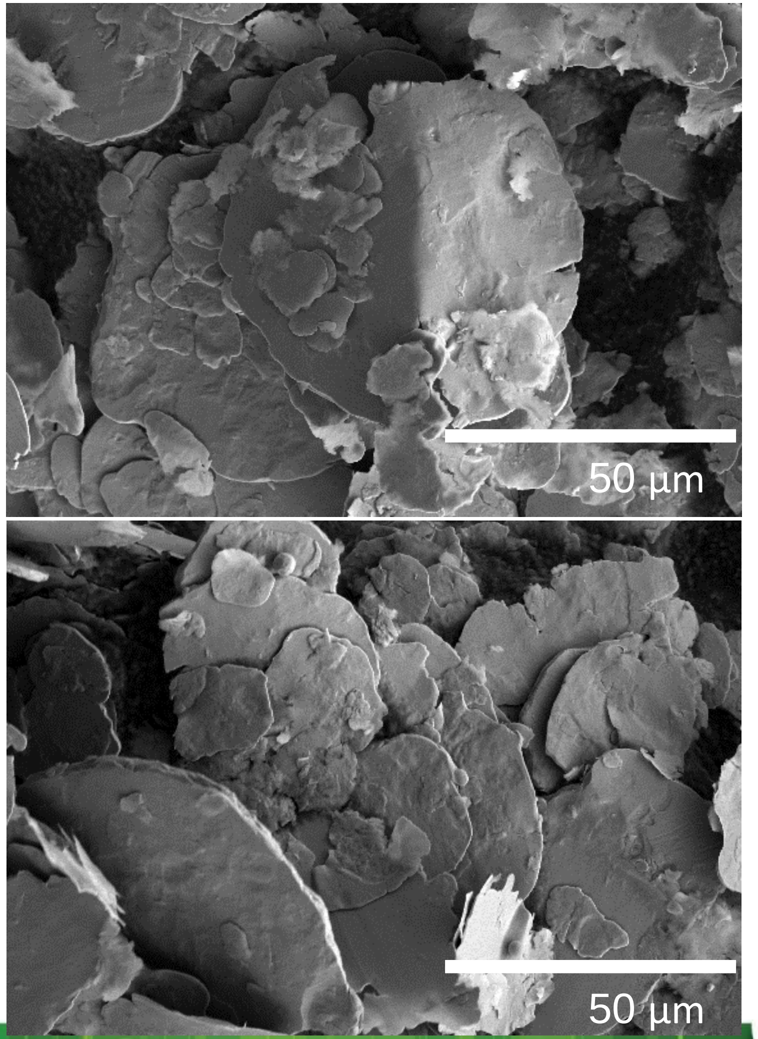
Cryomilled, Degassed, and Sieved (-325 Mesh)



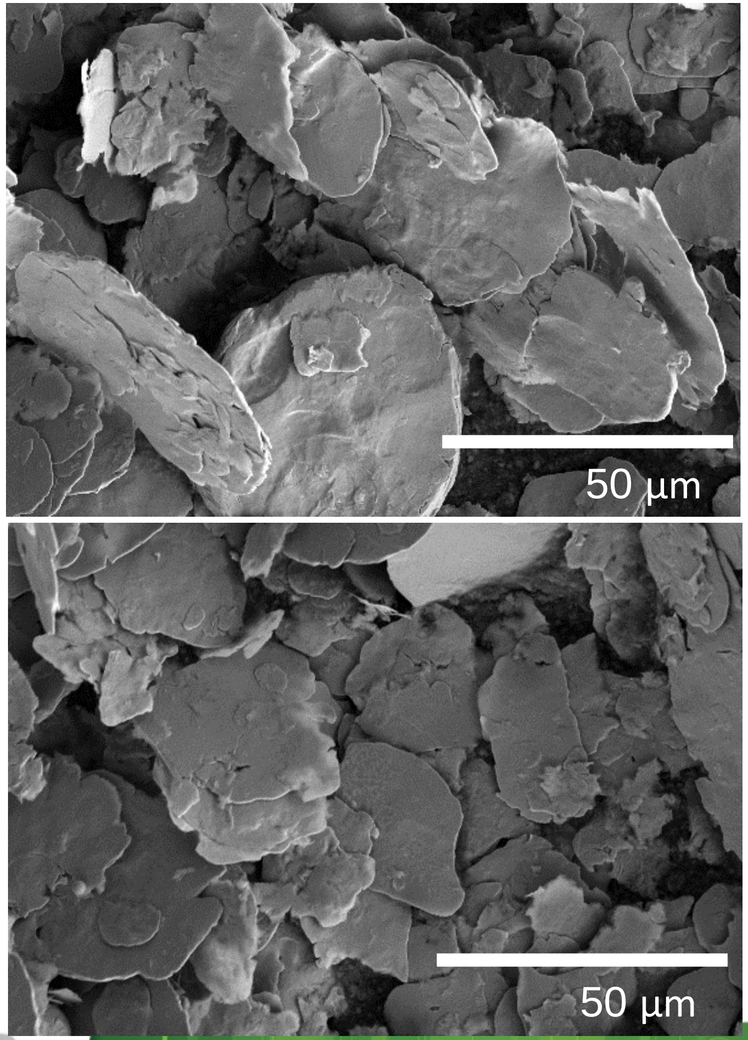


Cryomilled Powder: SEM

Cryomilled

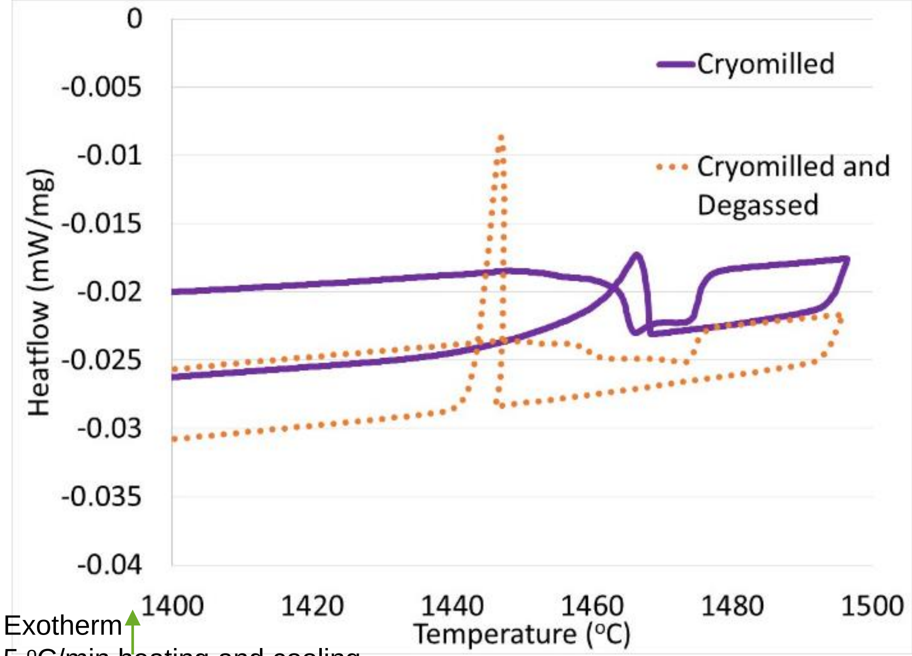


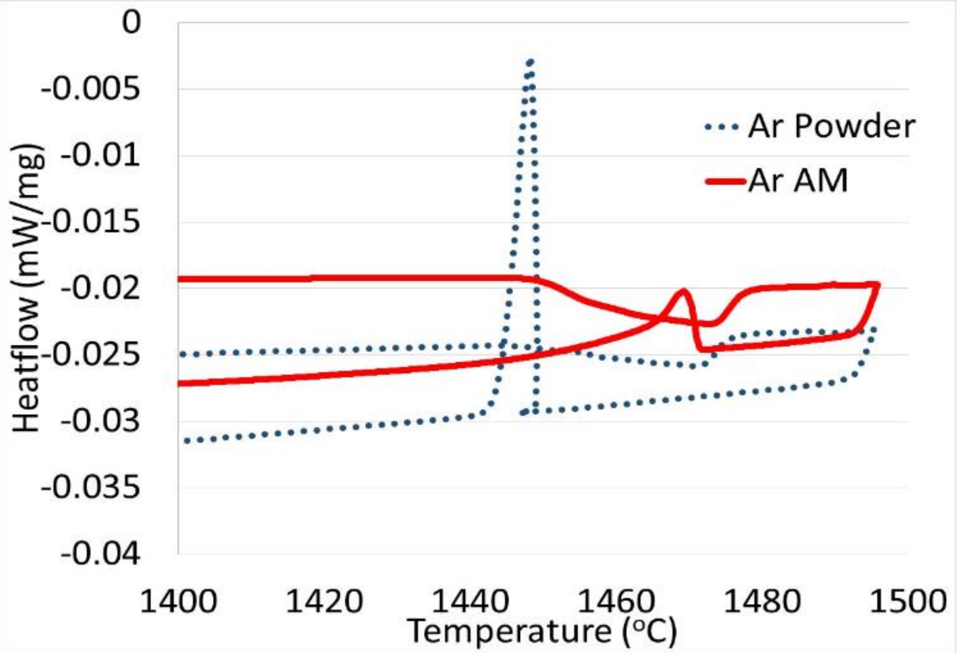
Cryomilled, Degassed, and Sieved (-325 Mesh)



Cryomilled Powder: DSC Analysis

In addition to solidification peak shift, cryomilled powder may have two melting peaks compared to the as-atomized powder.





Exotherm

5 °C/min heating and cooling

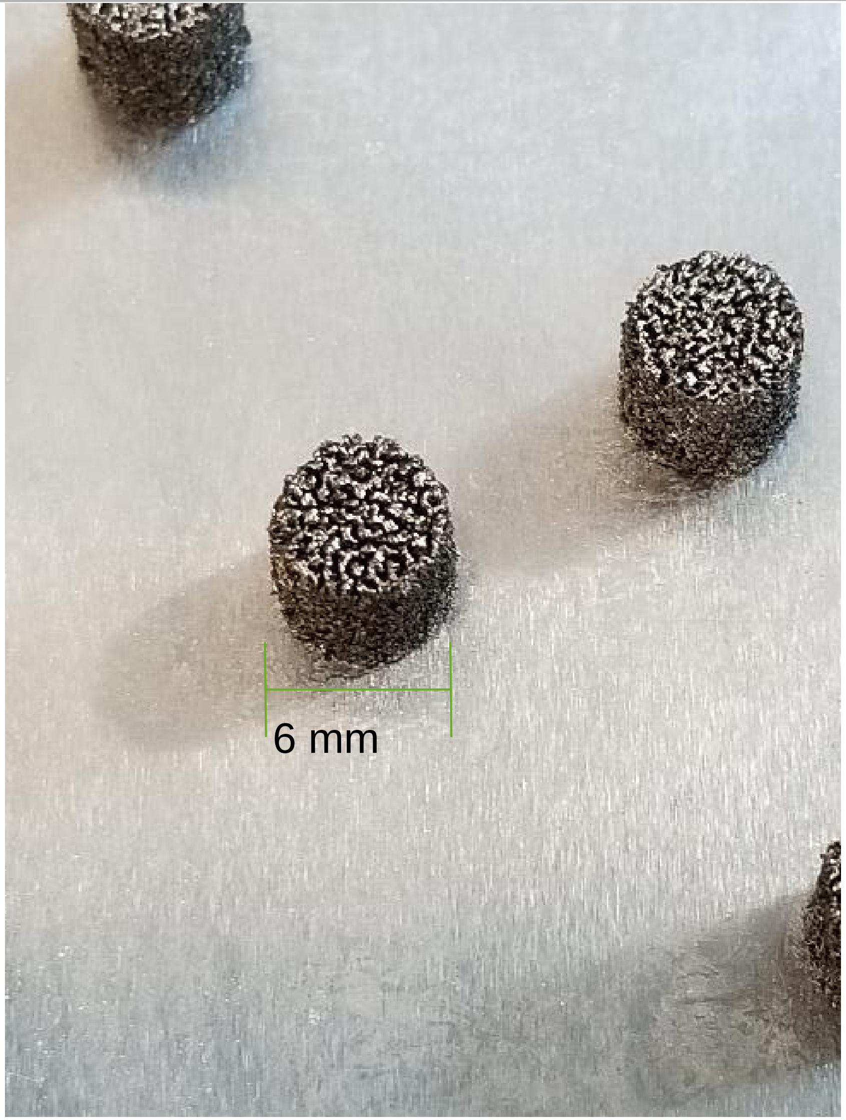
Cryomilled Powder Melting: 1463-1476 °C
Degassed Powder Melting: 1458-1473 °C
Cryomilled Powder Solidification: 1468 °C
Cryomilled and DG Solidification: 1448 °C

Powder Melting: 1448-1473 °C
As-Built Melting: 1450-1478 °C
Powder Solidification: 1450 °C
AM Solidification: 1472 °C

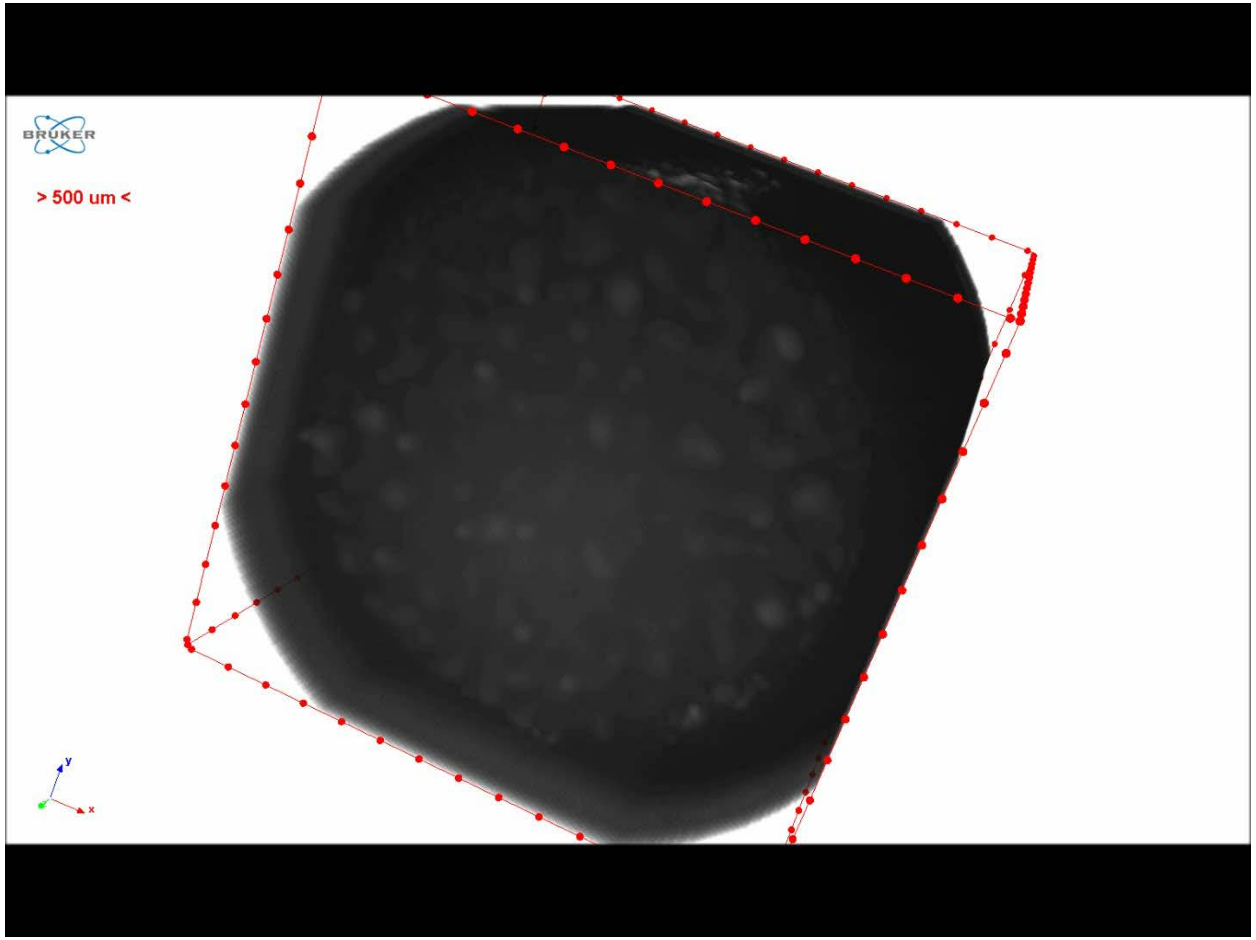
Cryomilled Feedstock: AM Build

As-built:

we have foam?

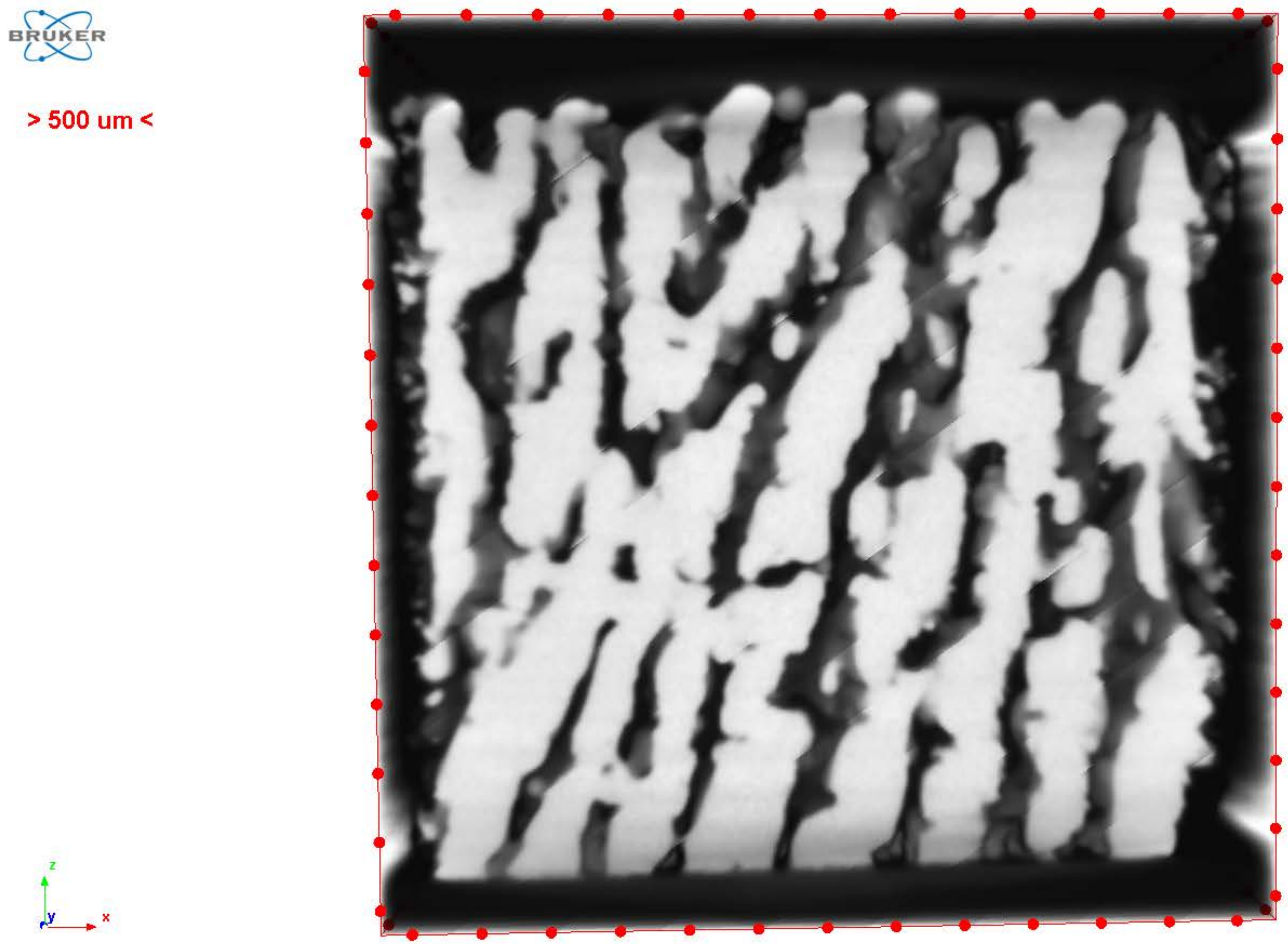


CM Feedstock: CT



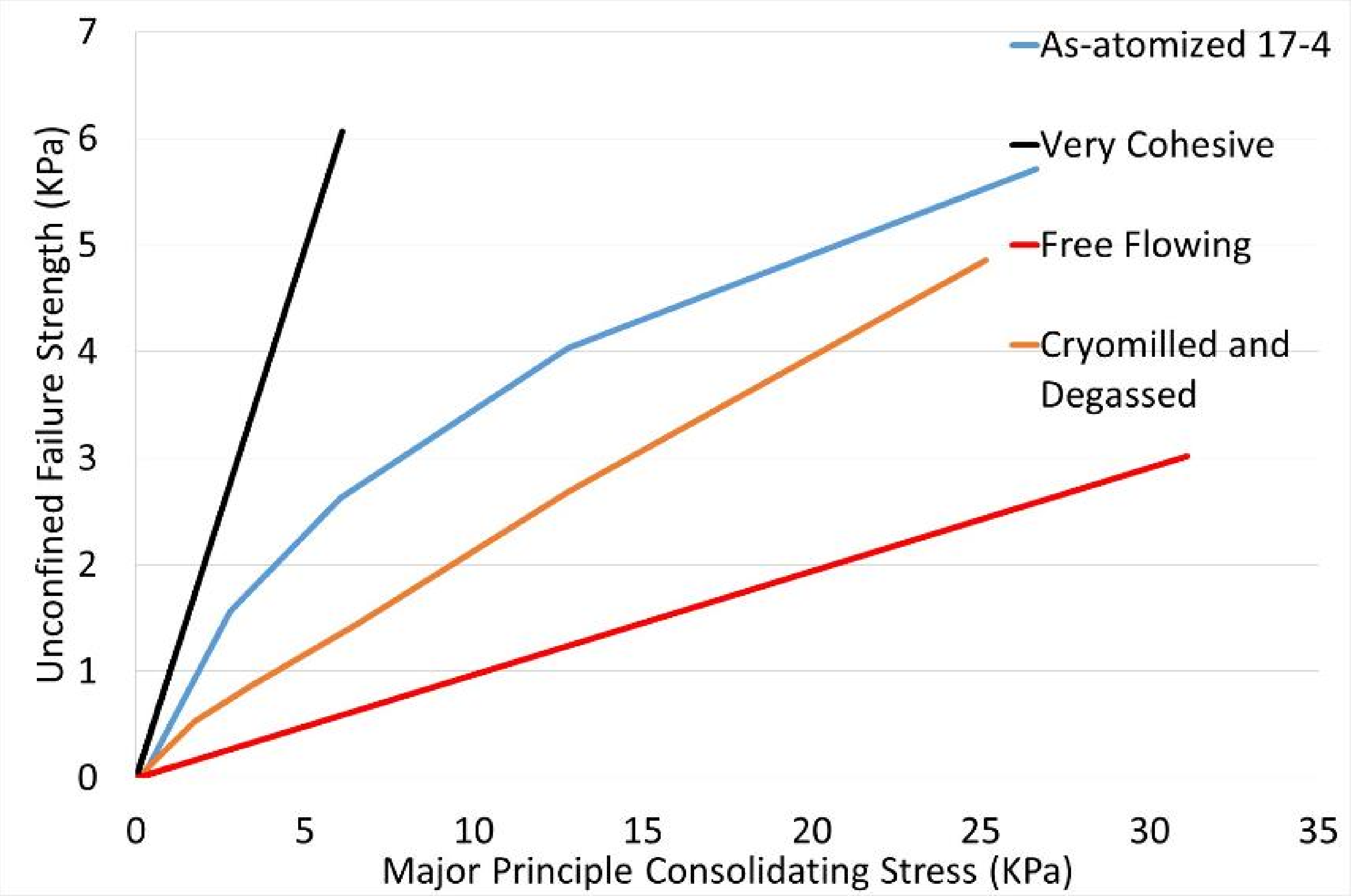
Cylinder was ~60% dense, ~40% porosity.

- ~35% open porosity
- Porosity measured with 2-D slices and may under-represent open porosity.



CM Feedstock: Brookfield Powder Flow

- Why so porous?
  - Poor powder recoating the build plate due to higher-than-expected flowability.
- Powder flow was measured after AM.
  - Unused powder was tested.
- DG-CM powder was more free flowing than as-atomized.



Conclusions

- **Despite porous nature, samples survived removal from the build plate without crumbling or falling apart.**

- **Open porosity suggests possible uses as a metallic foam.**
  - With increased milling time leading to nanostructuring, the potential exists to make nanograined metallic foams with improved strengths.

- **Cryomilling can be used to improve powder flowability.**
  - Plate-shaped particles are not expected to flow as well as spherical particles (surface chemistry effects?).

Conclusions

How to Fix (?)

- Slower Laser Travel Speeds - Increase energy density while decreasing pressure on the powder
- Increased Layer Thickness - Better powder coverage
- Higher Energy/Longer Milling Times - Different particle morphology
- Changes to PCA Amounts/Type - Different agglomeration
- Post CM Treatments - Plasma spheriodization
- Powder Mixes - Mix with as-atomized 17-4

- After 2 hours of cryomilling in liquid nitrogen, the resultant samples after AM changed buildability.
- Two hours of milling significantly changed the powder morphology, leading to improved flow.

What's Next?

Milling Process Optimization

- Milling Time - 2, 4, 8, hours +(?)
- Energy - Higher mill RPMS=Higher Energy=more break-up=less flaky(?)
- PCA - Selection: is stearic acid best?
  - Amounts
  - Degassing parameters
- Cryogen Selection - Liquid N_2 vs. liquid Ar
- Plasma Spheriodization?

AM Optimization

- AM parameter changes - laser travel speed, increased layer thickness
- Different AM techniques or parameters?

Acknowledgments

- Dr. Michael Kornecki for CM and XRD operations

- Dr. Jian Yu for powder flow measurements

The research reported in this document was performed in connection with contract/instrument W911QX-16-D-0014 with ARL. The views and conclusions contained in this document are those of SURVICE Engineering and ARL. Citation of manufacturer's or trade names does not constitute an official endorsement or approval of the use thereof. The U.S. Government is authorized to reproduce and distribute reprints for Government purposes notwithstanding any copyright notation hereon.

The research reported in this document was performed in connection with contract/instrument W911QX-17-C-0021 with ARL. The views and conclusions contained in this document are those of Bowhead Science and Technology and ARL. Citation of manufacturer's or trade names does not constitute an official endorsement or approval of the use thereof. The U.S. Government is authorized to reproduce and distribute reprints for Government purposes notwithstanding any copyright notation hereon.

Research was sponsored by the U.S. Army Research Laboratory and was accomplished under Cooperative Agreement Number W911NF-16-2-0008. The views and conclusions contained in this document are those of the authors and should not be interpreted as representing the official policies, either expressed or implied, of ARL or the U.S. Government. The U.S. Government is authorized to reproduce and distribute reprints for Government purposes notwithstanding any copyright notation herein.

Questions?

Contact Information:

- Frank Kellogg
- Franklin.R.Kellogg.CTR@mail.mil
- Frank.Kellogg@Survice.com
- 410-306-0803

The ARL AM Metals Team: Brandon McWilliams, Kyu Cho, Andelle Kudzal, Jennifer Sietins, Clara Mock, Bill Green, Jessica Sun, Mackenzie Perry, Christian Gobert, Ryan Rogers, Josh Taggart-Scarff, and Ricky Rapposeli

DSIAC
4695 Millennium Drive
Belcamp, MD 21017
443-360-4600
contact@dsiac.org