Refractory Alloy Additive Manufacture Build Optimization (RAAMBO)

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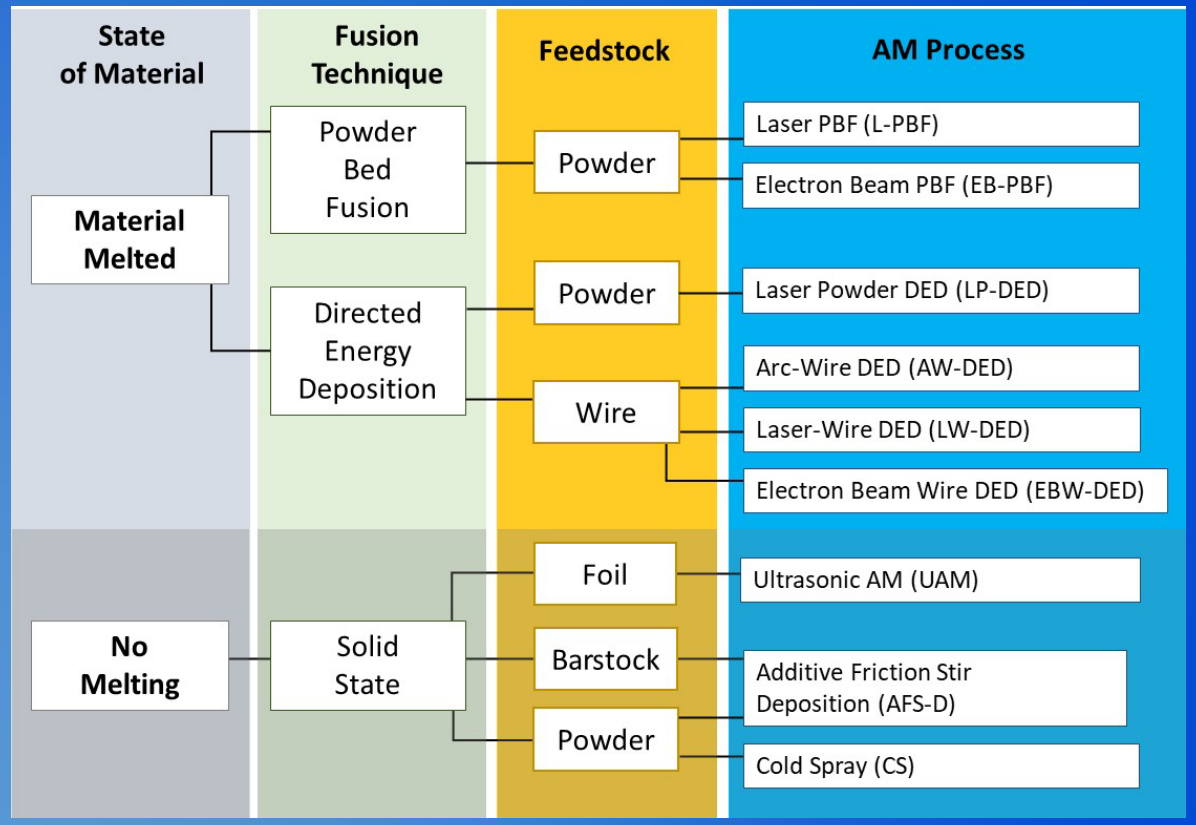
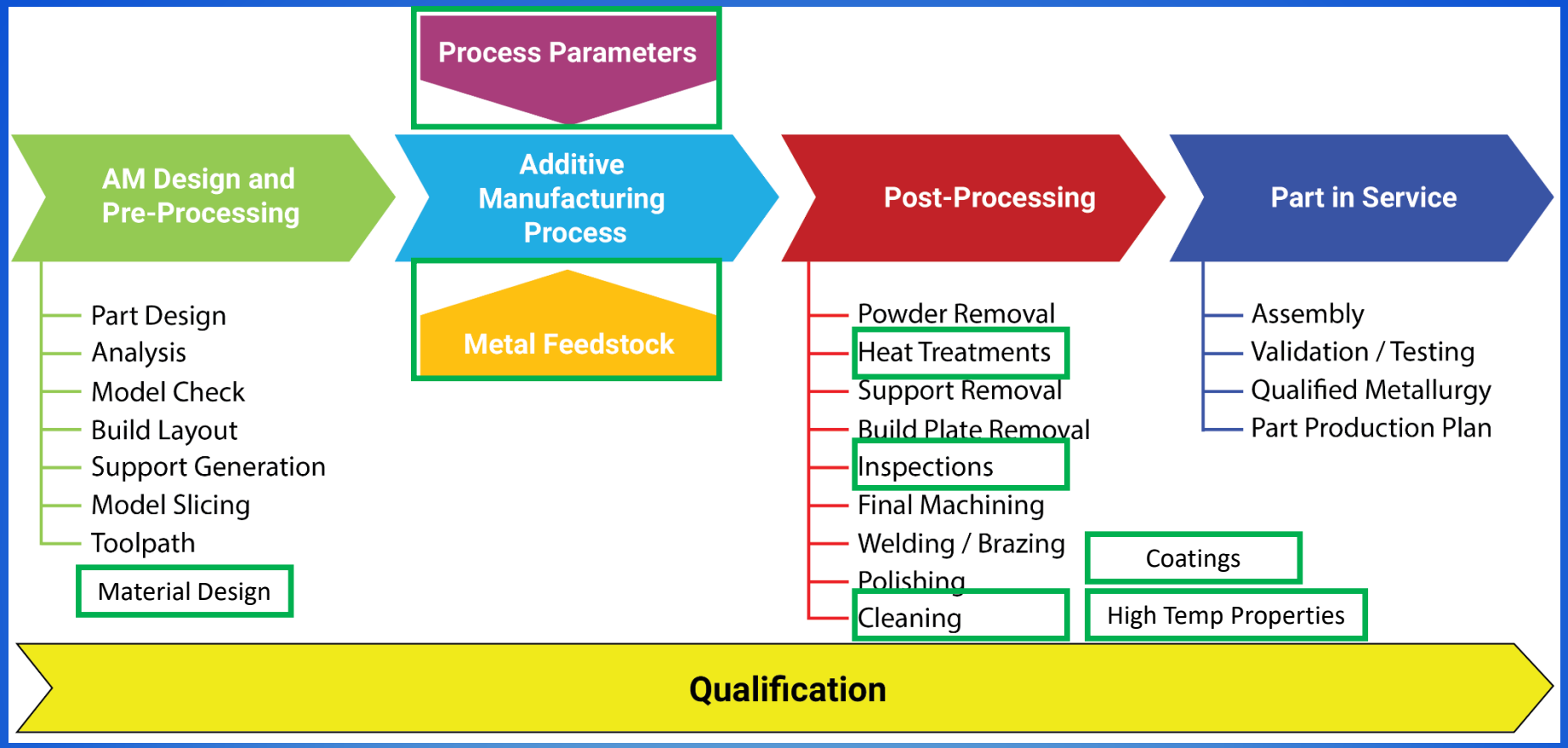
Background: Additive Manufacture (AM) Process Options

- Appropriate Application
  - High complexity & difficult to manufacture
  - Low production rate
  - Long lead time & high cost
- Advantages
  - Increased design flexibility
  - Near net-shape complex geometry
  - Part count reduction
  - Performance improvement (e.g. weight reduction)
  - Rapid design-fail-fix cycles
  - One-off and discontinued parts
  - Reduced scrap (lower buy-to-fly ratio)
  - Reduced lead time and cost



Background: AM Process



Iterative AM Lifecycle. Courtesy Gradl, et al., 2021.

Background: Refractory Metals

- Refractory metals and alloys are used for service in extreme high temperature environments:
  - Reaction Control System (RCS) thrusters.
  - Space Nuclear Propulsion (SNP) clad and structure.
  - Hypergolic / green propulsion chambers and catalyst.
  - Electric propulsion grids.
  - Power conversion system heat pipes and regenerators.
  - Hypersonic wing leading edges.

- Refractory metals are desirable due to:
  - High melt temperature (T_m).
  - Retain strength and hardness at elevated temperature.

- Aerospace refractory metal parts tend to be:
  - Thin wall geometries (converging-diverging nozzles).
  - Relatively simple geometries.
  - High buy-to-fly ratio (20:1 to 50:1).
  - Low production rate.

Apollo CSM RSC using C103. Courtesy Aerojet-Rocketdyne

Green propulsion Re thruster.

TZM alloy heat pipe. Courtesy Advanced Cooling Technologies.

Base	Name	Composition (wt%)
Nb	Nb	Nb
	Nb-1Zr	Nb-1Zr
	C103	Nb-10Hf-1Ti
	C129Y	Nb-10Hf-10W-0.1Y
	Cb752	Nb-10W-2.5Zr
	C3009	Nb-30Hf-10W
	WC3015	Nb-28Hf-13W-5Ti-2Ta-1Zr
	FS85	Nb-28Ta-10W-1Zr
Mo	Mo	Mo
	Mo-21Re	Mo-21Re
	Mo-41Re	Mo-41Re
	Mo-44Re	Mo-44Re
	Mo-47.5Re	Mo-47.5Re
	TZM	Mo-0.5Ti-0.08-Zr-0.2C
W	W	W
	W-25Re	W-25Re
Ta	Ta	Ta
	Ta-10W	Ta-10W
Ir	Ir	
	DOP26	Ir-0.3W-0.006Th-0.005Al
Re	Re	Re

Traditional Refractory Alloys

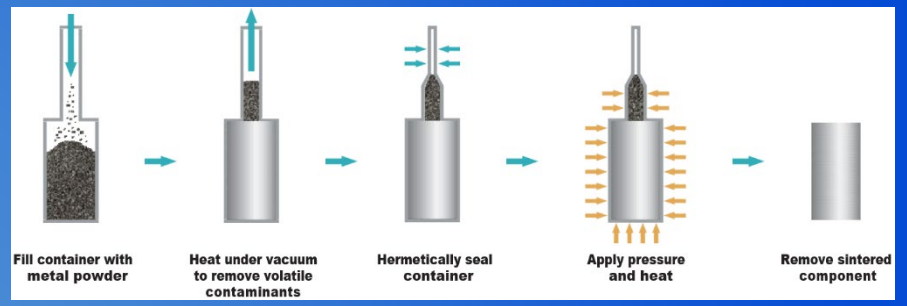
X-51A hypersonic test vehicle. Courtesy USAF.

Problem

- Traditional refractory manufacture is difficult and expensive:
  - Bar, plate, tube, sheet stocks and sizes limited (constrains design).
  - Powder feedstock are angular and not usually alloyed.
  - High feedstock cost.
  - Relatively difficult to form/machine (fracture prone).
  - Heat treatment requires specialized facilities (O, C, N sensitive).
  - Joining options limited (e-beam weld).
  - Inspection options limited.

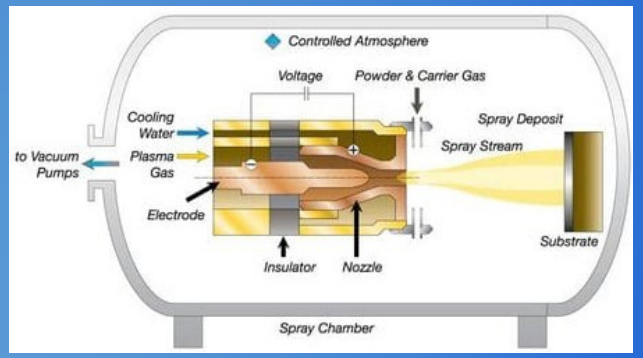
C103 forged bar stock. Courtesy ATI.

- Alloys designed for traditional manufacture:
  - Powder metallurgy (CIP, HIP, deposition).
  - Forging.
  - Wire and/or plunge EDM.
  - W ($100/kg) or Mo ($80/kg) alloyed with 25-47.5 wt% Re ($2.76k/kg) to improve ductility.

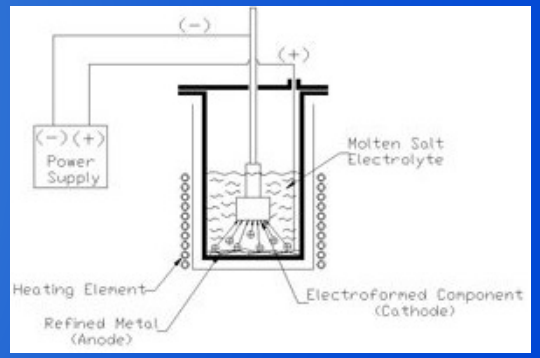


Hot Isostatic Press (HIP) process [1].

- Feedstock vendors limited
  - Angular/unalloyed powder does not meet AM specs.
  - Gas atomization methods limited by high T_m.



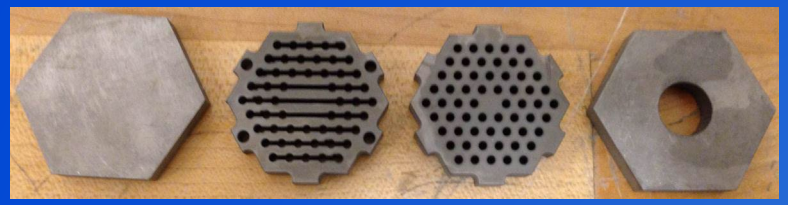
Vacuum Plasma Spray (VPS) process [2].



Electro Deposition / Forming process [3].

[1] https://www.malvernpanalytical.com/en/industries/advanced-manufacturing/powder-metallurgy/isostatic-pressing.
[2] https://www.neodynamiki.gr/
[3] https://plasmapros.com/processes/

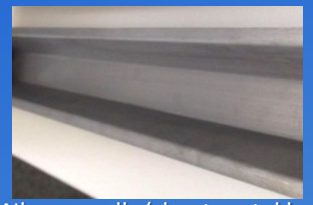
Traditional Manufacture Example: NTP Fuel



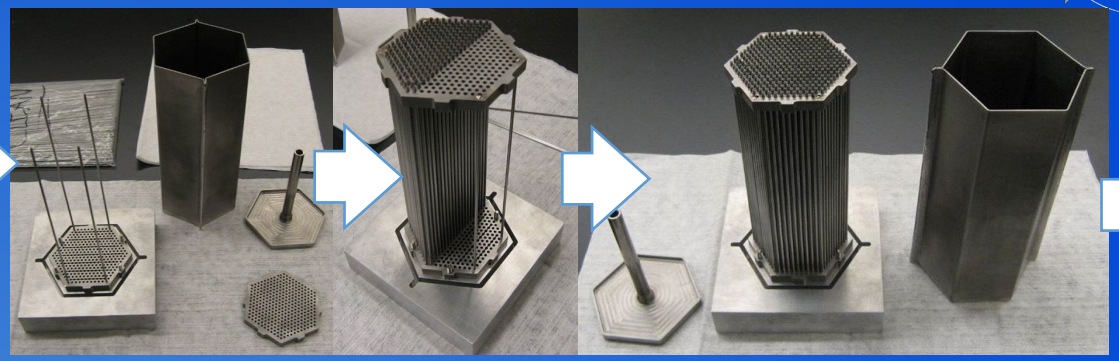
Nb can end-caps and spacer grids (water jet).

W clads (vacuum plasma spray).

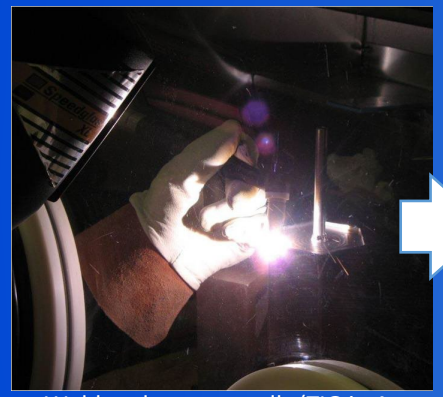
Mo rods coated with W (electro-form).



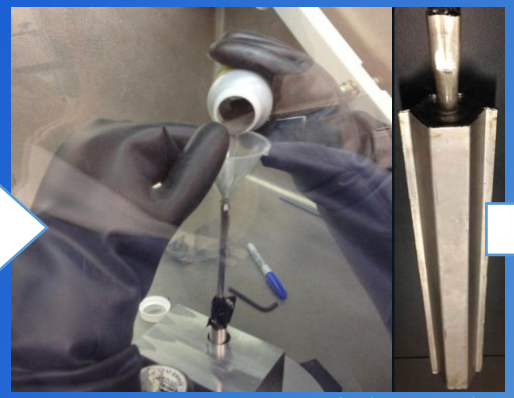
Nb can walls (sheet metal break).



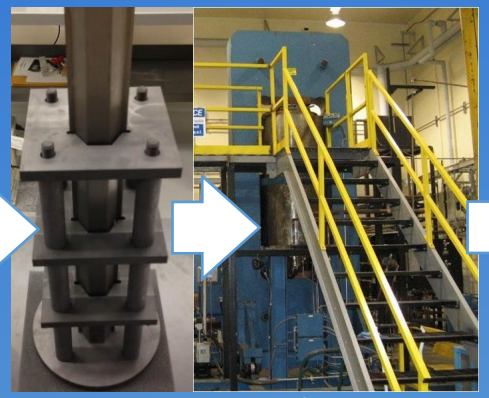
HIP can tooling and assembly process.



Weld end caps to walls (TIG in Ar glovebox).

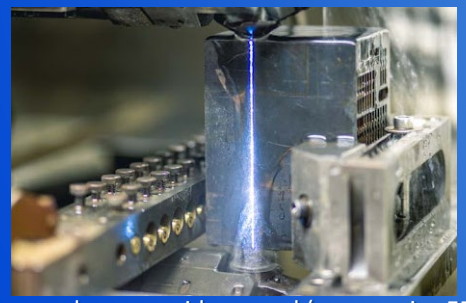


Swage, leak check, powder fill (~55 %RD), evacuate, crimp/weld/cut fill stem.



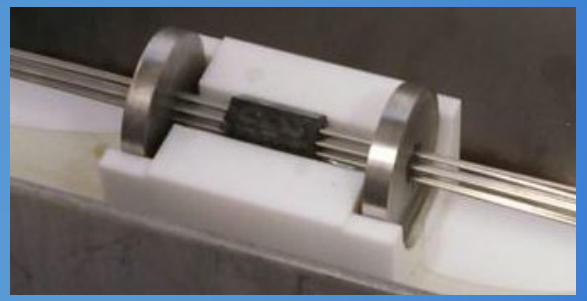
Graphite tooling and HIP furnace schedule.

HIP part consolidation to >99 %RD, geometric distortion, wall cracking.

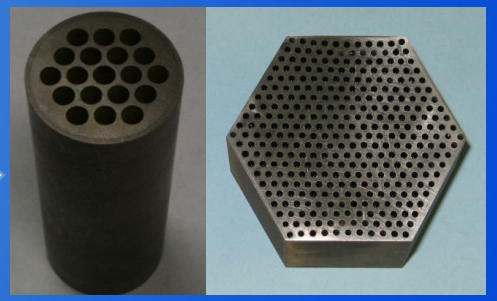


End cap and spacer grid removal (saw or wire-EDM).

HIP can removal (surface grinding).



Chemical etch to remove Mo mandrels.



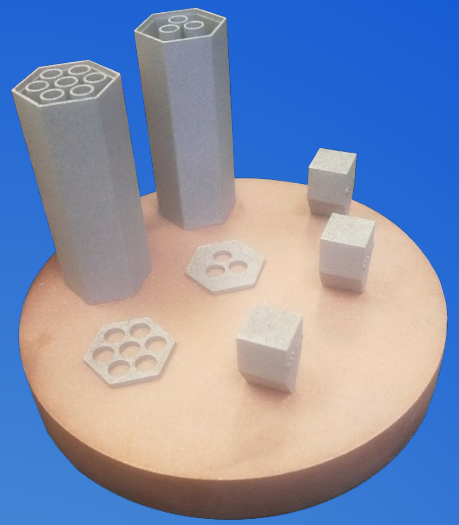
Cermet fuel segment.

Development Evolution

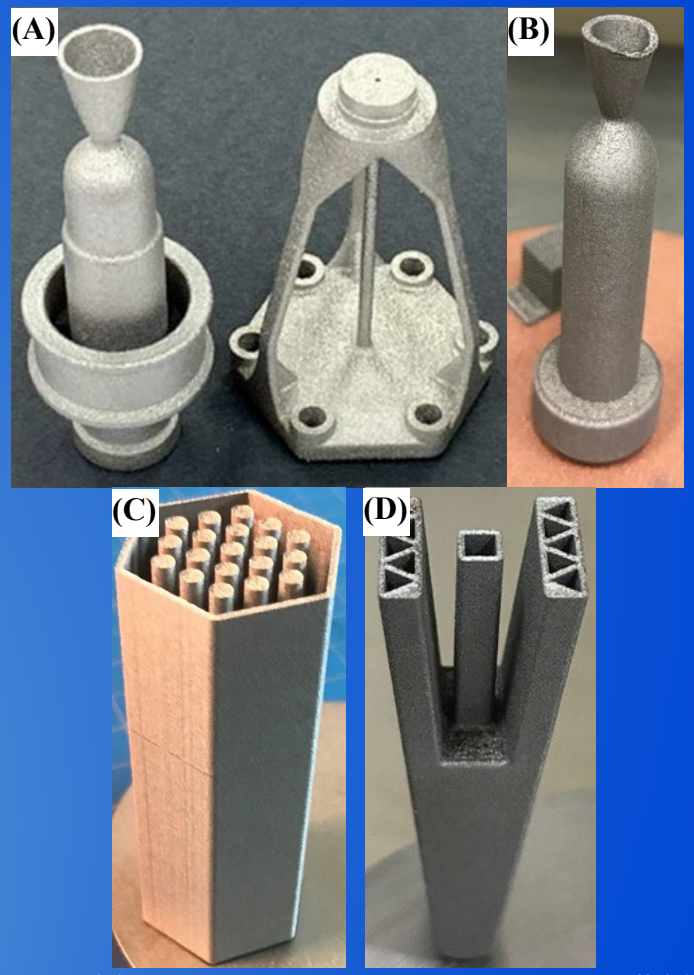
- Refractory manufacture at MSFC
  - NTP fuel development (FY11-present)

- Refractory AM demonstrated using:
  - Laser powder bed fusion (L-PBF)
  - Electron beam PBF (EB-PBF)
  - Laser powder DED (LP-DED)
  - Electron beam wire DED (EW-DED)

- Previous / Ongoing AM Investments
  - L-PBF AM C103 for propulsion (FY18 CAN* with Castheon).
  - L-PBF AM W ultra-fine lattices for propulsion (FY18 CAN with EOS).
  - Green propulsion development (FY19 CAN with UTEP).
  - Binder Jet AM ZrC for NTP (FY19 CAN with UTEP).
  - L-PBF AM W and Mo for NTP (FY19-FY22 GCD).
  - L-PBF AM W Hypersonic WLE (FY20 ARC)
  - L-PBF AM Mo Thruster & Ir Catalyst (FY21 CIF)
  - L-PBF AM W, Mo, C103 1 N Green Propulsion Refractory Thrusters (FY21 TE).
  - LP-DED AM C103 nozzle extension (FY21-22 GCD with RPMI).
  - Refractory High Entropy Alloy Development (FY21-23 ESI & EPSCoR).



First NASA W AM build: NTP fuel clad with integrated coolant channels.

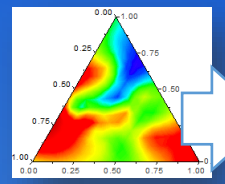


L-PBF AM (A) C103 1 N reaction chamber and thrust stand-off, (B) 1N AM W chamber, (C) AM W NTP fuel clad, (D) AM W hypersonic wing leading edge with integrated heat pipe channels.

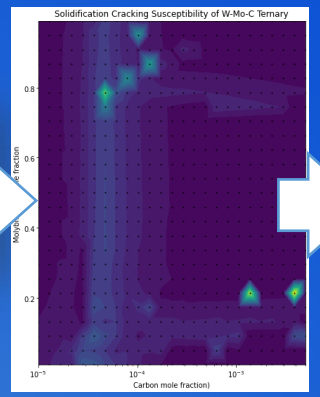
*CAN = Cooperative Agreement Notice

Material Design

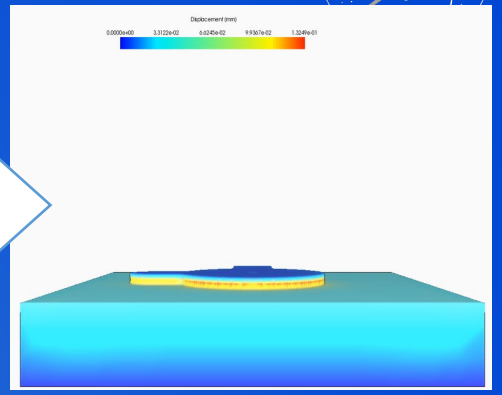
- Design AM-optimized refractory alloys
  - Integrated Computational Materials Engineering (ICME).
  - Melt/solidification transformation and dynamics, crack susceptibility, AM build simulation, and property prediction.



Alloy formulation

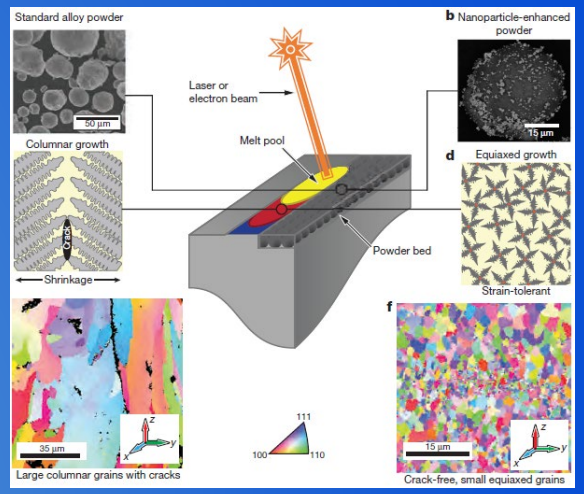


Crack susceptibility



Parameter prediction and simulation.

- Development Objectives
  - *Phase 1:* Utilize existing refractory options: W, Mo, C103, Re.
  - *Phase 2:* Dispersoid additions (nano-powder) to feedstock to reduce cracking and improve properties.
  - *Phase 3:* Design AM optimized formulations with emphasis on printability, properties, availability, and cost.



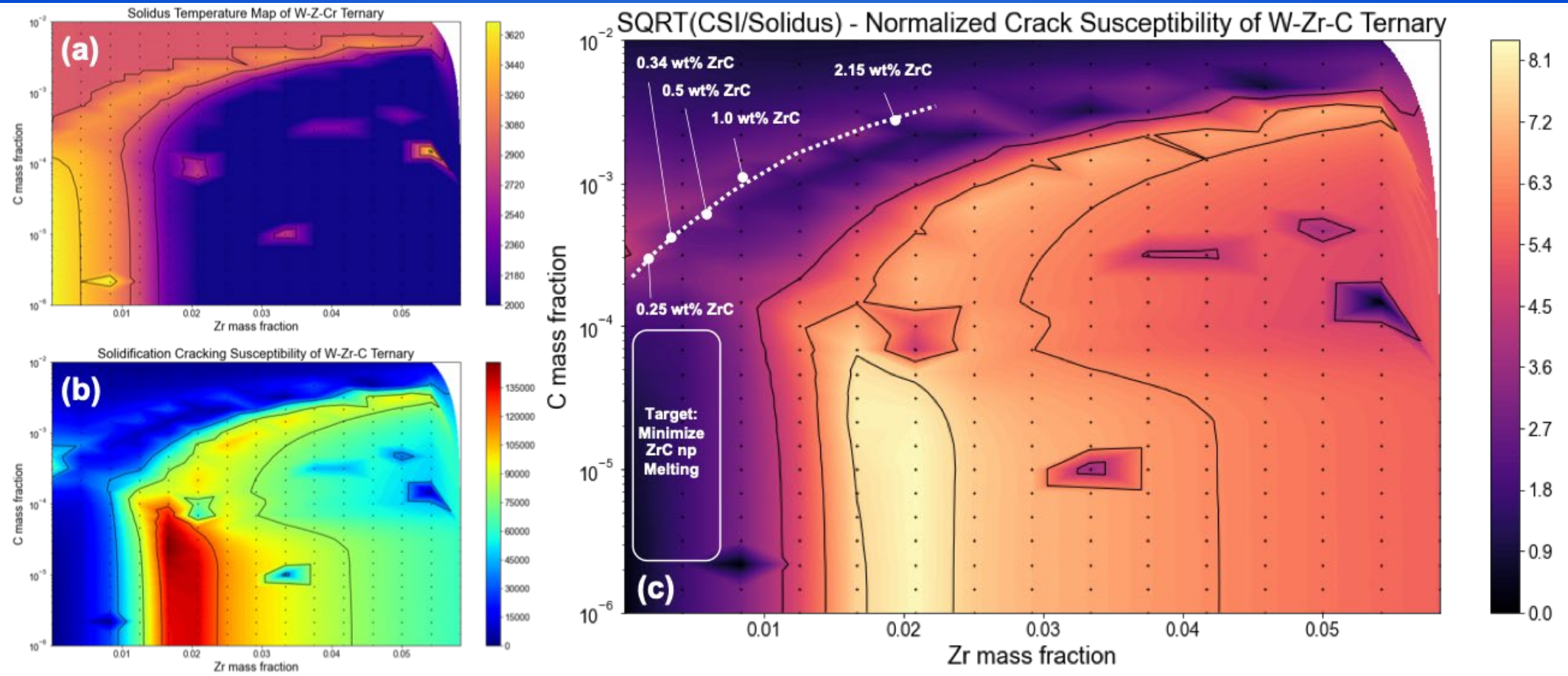
Nano-powder dispersoid stabilization and strengthening [1].

- Timeline
  - FY22: L-PBF AM of W, Mo, C103, dispersoid formulations.
  - FY23-FY24: LP-DED C103, W-xRe, Mo-xRe, FS85, WC3009, WC3015.

RHEA specimen characterization. Courtesy TAMU.

[1] Martin, J., et al., "3D Printing of high-strength aluminum alloys," Nature, Vol 549, 2017, pp 365-370.

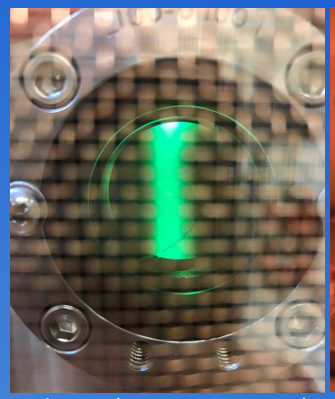
ICME Example: Dispersoid Optimization W-ZrC



Three contour plots of the W-Zr-C ternary system computed with custom Python algorithms are shown. Figure (a) shows the solidus temperature, an important data point for mechanical property design, resulting from non-equilibrium Scheil solidification ($D_L = \infty$, $D_S = 0$). Figure (b) shows Kou's crack susceptibility index (CSI) mapped for this ternary system. A higher value of CSI indicates greater susceptibility to hot cracking. An optimization will produce the most desirable alloy by maximizing solidus temperature, (a) to increase mechanical stability to highest temperature possible, and by minimizing the CSI, (b). For example, a normalization of the CSI by solidus temperature shows regions of interest (c). Additions by mass of stoichiometric ZrC are shown in (c).

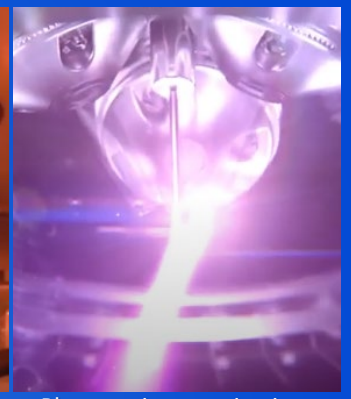
Powder Production

- Refractory Metal Powder Production Options
  - Nano dispersoid additions: MSFC acoustic mixing.
  - Plasma spherodization: MSFC Tekna Tek15.
  - Electrode Induction Gas Atomization (EIGA): TBD.
  - Reuse/Recycling: 6K Additive, MolyWorks, TBD.
- AM Powder Specifications
  - Alloyed elements
  - Spherical morphology
  - Fully dense particles (>99.9 %TD)
  - Particle size distribution (PSD):
- AM Grade Powder Options
  - Elemental: W, Mo, Nb, Ta, Re.
  - Alloys: C103, FS85, WC3009 (dev), WC3015 (TBD), MoxRe (dev), WxRe (dev).

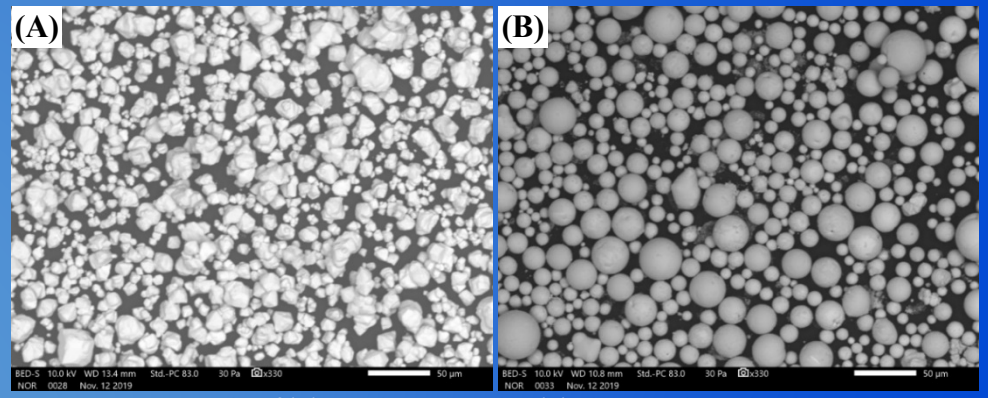


Plasma (RF or microwave) spheroidization.

EIGA of ingot. Courtesy Sandvik.



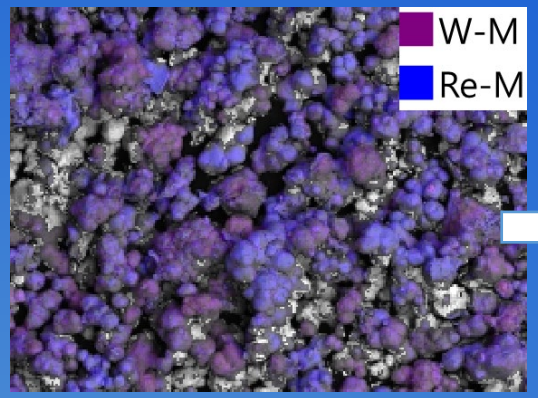
Plasma wire atomization. Courtesy GE AP&C.



SEM micrographs of (A) angular W powder, (B) plasma spheroidized W powder.

Demonstration Scale Powder Production Example

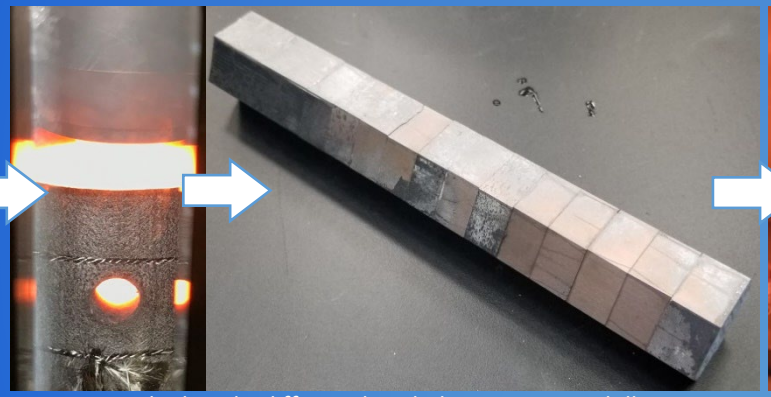
- Direct Current Sinter (DCS)
  - Low-cost lab scale using existing equipment.
  - Process development at MSFC DCS-25.
- EIGA
  - DCS billet atomized into alloyed powder.



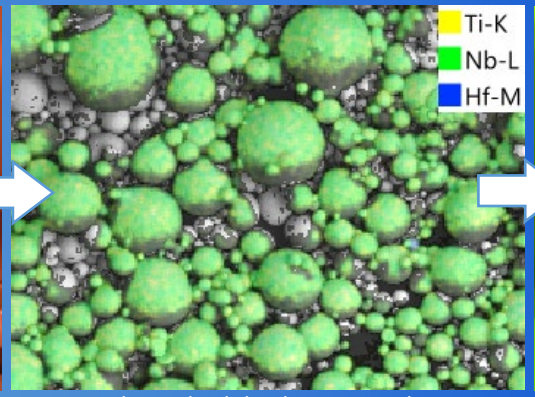
Mixed elemental angular powder.


MSFC Thermal Tech DCS-25 furnace consolidates powder into pucks and heat treatment to solid-solution.

DCS pucks Ø40 mm x t15-25 mm (potential for >Ø60 mm).


Stacked pucks diffusion bonded via DCS into a billet.


Billet converted into powder with EIGA.

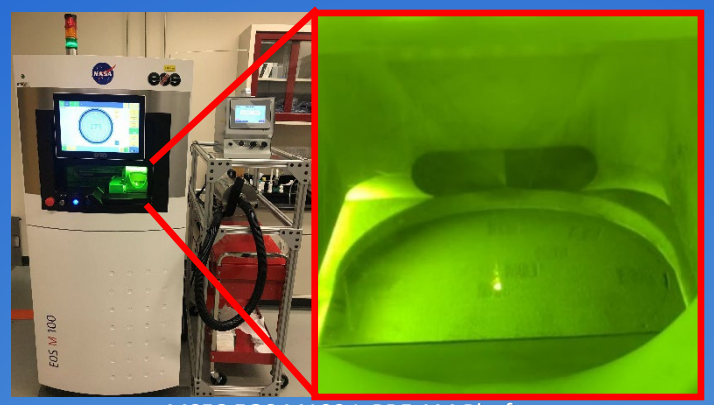


Spherical solid-solution powder.

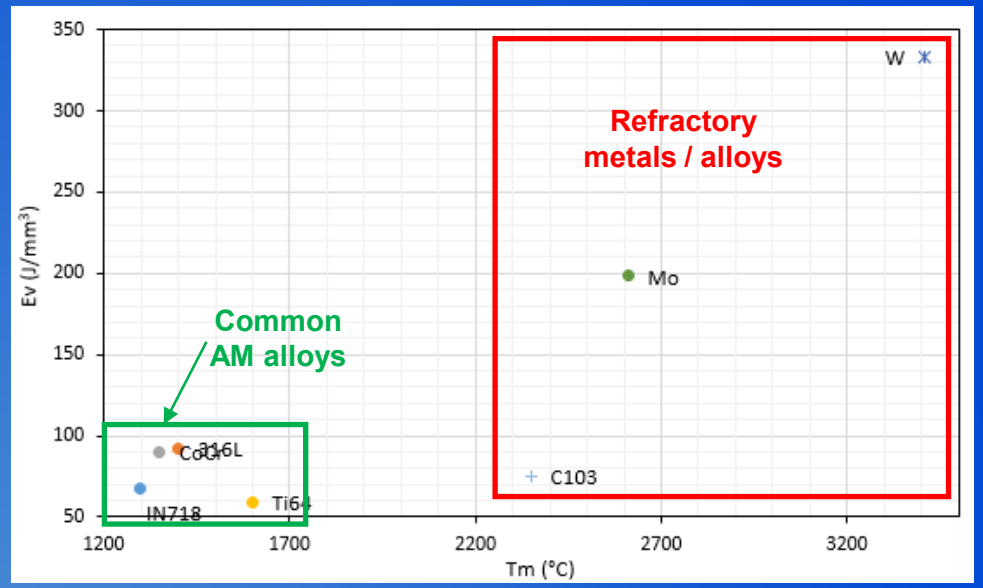

L-PBF AM parameter development.

L-PBF & LP-DED AM Parameter Development

- L-PBF parameter development
  - Computational predictions drive experimental iteration.
  - Resulting parameters fed back for build simulations.
  - Small platforms minimize powder costs, easy material change, small demo part production.



MSFC EOS M100 L-PBF AM Platform.



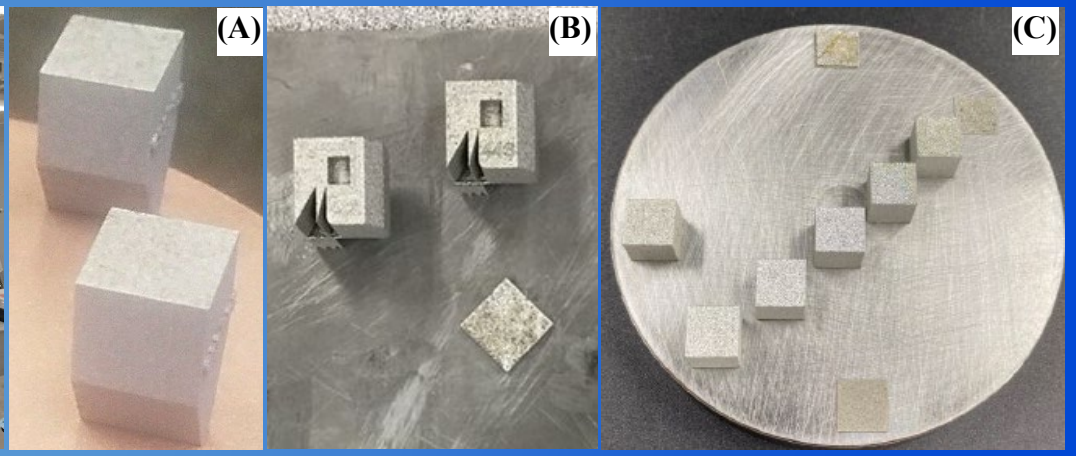
Melt Temperature vs. L-PBF energy density map.

- Build Plate options
  - W: 304 SS, W, CU110
  - Mo: Mo, Ti6Al4V
  - C103: Nb, C103, Mo, Ti6Al4V

- Process Gas
  - Ar (O_2 and H_2O < 10 ppm) or Ar- 3vol% H_2.

- LP-DED Parameter development
  - RPM Inc. currently developing C103.
  - UTEP CAN develop Nb and C103.
  - Topology optimized nozzle extension demonstration article test in FY23.

UTEP RPMI Inc 222XR LP-DED AM Platform.



L-PBF AM metallographic specimens in (A) W, (B) C103, (C) Mo.

Heat Treatment Optimization

- Stress Relief
  - W: 1100-1200 °C for 1 hr in vacuum of $1x10^{-4}$ Torr.
- Hot Isostatic Press (HIP)
  - W: 1700-1800 °C from 172-193 MPa for 1-4 hrs [1]
  - Max furnace temperatures likely inadequate.
- Recrystallization
  - W: 1250-1350 °C for 1 hr in vacuum of $1x10^{-4}$ Torr.
- Sacrificial Wrap
  - O, N, C sensitive metals (e.g. Nb, Mo, Ta) must be foil wrapped during heat treatment even with UHP argon.
  - Sacrificial foil wrap should have a high T_m with an affinity for O, N, and C (e.g. Ta or Nb).
  - If the foil exhibits excessive brittleness after heat treat replace with new foil wrap prior to subsequent heat treatments.

MSFC vacuum furnace.

MSFC large HIP furnace.

Alloy	T_m (°C)	$0.7T_m$ (°C)
AlSi10Mg	580	406
IN718	1247	873
IN625	1295	907
CoCrMg	1350	945
316L SS	1375	963
Ti6Al4V	1600	1120
GRCop42	1750	1225
C103	2350	1645
Mo41Re	2428	1700
Mo	2610	1827
Ta	3017	2112
W25Re	3050	2135
Re	3185	2230
W	3410	2387

HIP temperature constraints.

[1] Noto, H., et al., "Microstructure and Mechanical Properties of Dispersion Strengthened Tungsten by HIP Treatment Followed by Thermal Annealing, Results in Materials, Vol. 7, 2020 100116.

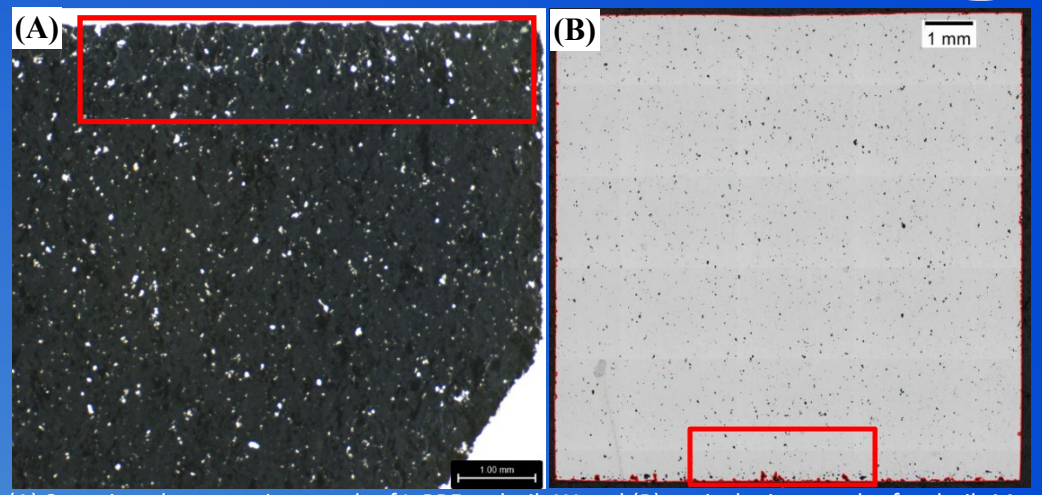
Joining

- Electron beam weld development
- Variables
  - Materials: C103, Nb, Mo, Re, W and CDS variants
  - L-PBF and LP-DED specimens
  - Joint design
  - Stress relieved and HIP conditions
  - Machined surface finish
- Weld Inspection
  - X-ray CT when possible
  - Die penetrant
- Weld Microstructure Characterization

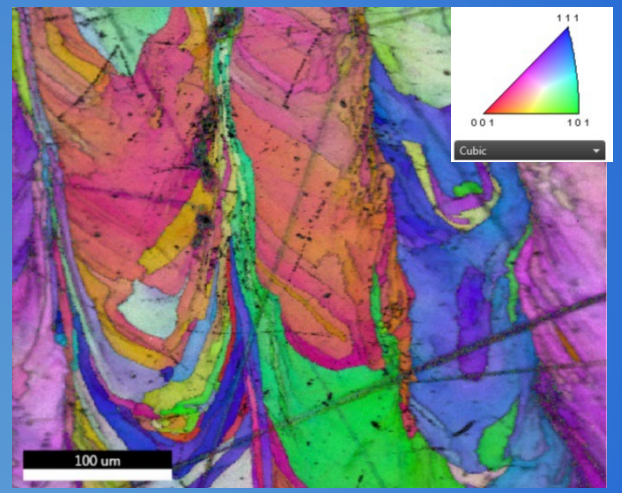
MSFC electron beam welder.

Characterization

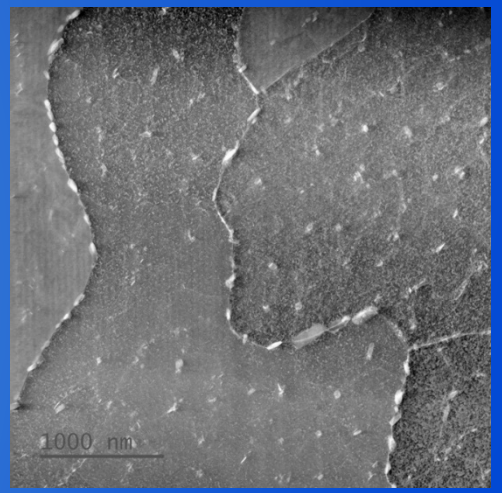
- Optical Microscopy
  - Morphology, optical density, porosity.
- Density Measurements
  - Archimedes, optical, He pycnometry
  - Typical L-PBF AM cutoff 99.5 %RD
  - L-PBF am W 93-95 %RD
  - L-PBF AM Mo 97.9 %RD
- SEM/EDS
  - Morphology, elemental distribution
- EBSD
  - Grain size and orientation
- TEM
  - Dispersoid distribution, precipitates from HT.
  - University of Alabama.



(A) Scanning electron micrograph of L-PBF as-built W and (B) optical micrograph of as-built Mo.



EBSD IPF+IQ of as-built L-PBF C103 grain orientation and size.



TEM micrograph of L-PBF AM as-built C103 HfO_2 precipitate distribution.

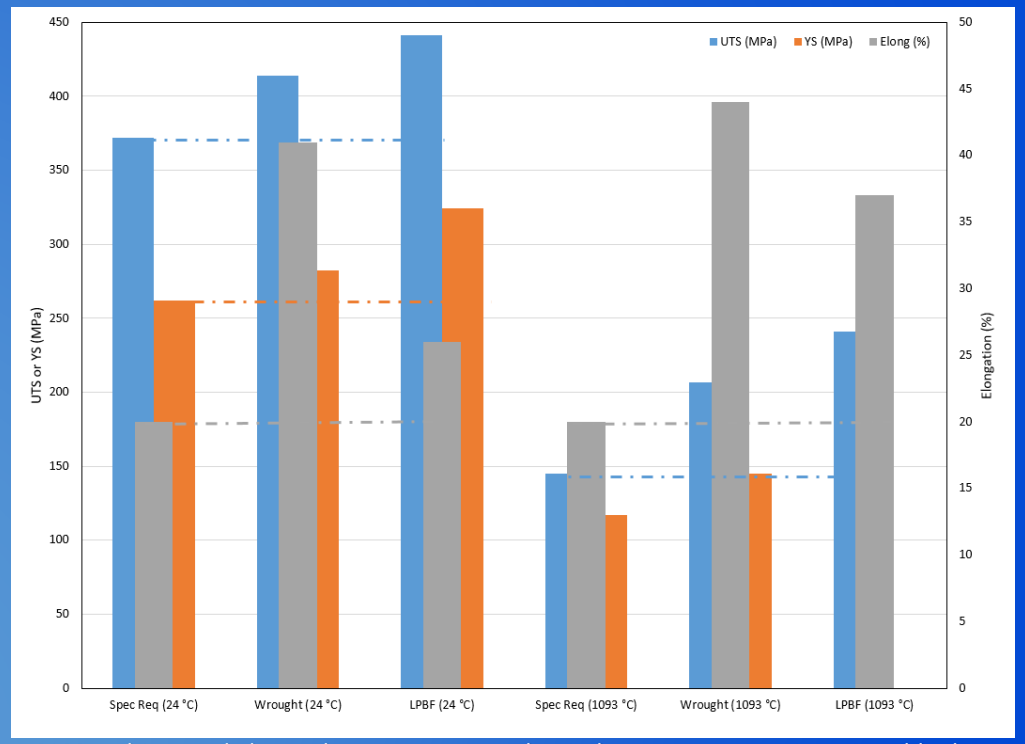
Mechanical Testing

- Extremely limited options
- Tensile Testing (20 °C)
  - Psylotech meso-scale loadframe.
  - ASTM E8 modified mini tensile specimens.
  - Micro-cracks have significant impact on mechanical properties.
- Limited Tensile Testing options
  - Ohio State University CAN: Gleeble (1500-2500 °C)
  - Westmorland: (1200 °C, air)
  - Touchstone Labs: (1500 °C, air)
  - Southern Research: (2500 °C, graphite tooling)
  - GRC procuring high temperature, high vacuum load frame capable of tensile, LCF.
- Creep Testing (1500-2000 °C)
  - GRC study to refurbish existing test frames.
  - Westmorland.

Tensile data of L-PBF AM W at 20 °C.

Condition	UTS_m (MPa)
As-Built	157.65 ± 17.9
Stress-Relieved	164.34 ± 29.7
Recrystallized	177.30 ± 4
HIP*	177.44 ± 81.5
Wrought	349.26

*Furnace Tmax achieved recrystallization but insufficient to induce densification.

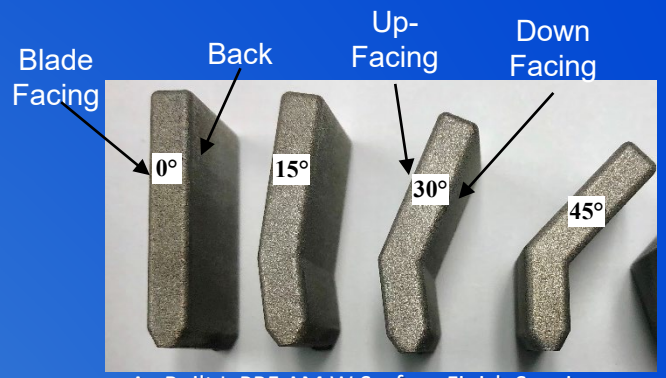


C103 ambient and elevated temperature mechanical property comparison. Possible that fine distributed oxides from the L-PBF acts as a strengthener and stabilizer.

Surface Finish & Coatings

- Surface Finish Enhancement
  - Chemical Milling (CM): TechMet.
  - Chemical Mechanical Polish (CMP): REM Surface.
  - Electropolish: Voxel Innovations, Faraday Technology.

AM surface finish specimens vs. condition.

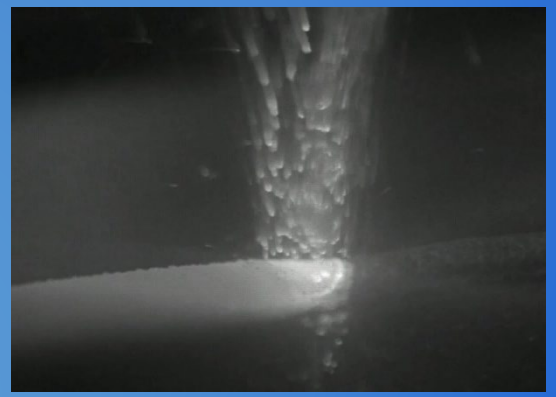


As-Built L-PBF AM W Surface Finish Specimens

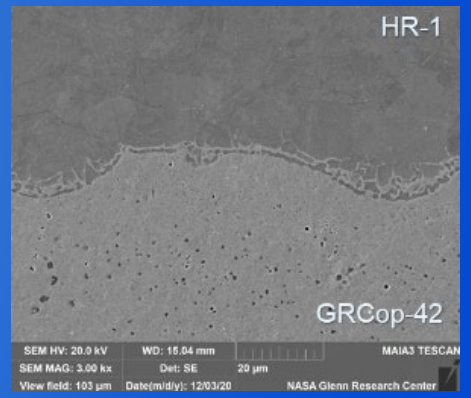
Surface Finish of As-Built L-PBF AM W

Condition	S_a (µm)								
	0° (vertical)		15°		30°		45°		90° (horiz)
	Blade-Facing	Back	Up-Facing	Down-Facing	Up-Facing	Down-Facing	Up-Facing	Down-Facing	Up-Facing
W As-built	5.5	6.3	5.4	7.3	6.1	8.9	9	15.7	-

- Protective Barrier Coatings
  - External surfaces = feasible.
  - Internal surfaces = difficult.
  - R512E (Si-20wt%Fe-20wt%Cr) slurry diffusion bond: Himetco.
  - Iridium CVD: Ultramet.
  - $MoSi_2$ thermal spray: Plasma Processes.
  - LP-DED: RPMI Inc, UTEP, Formalloy.



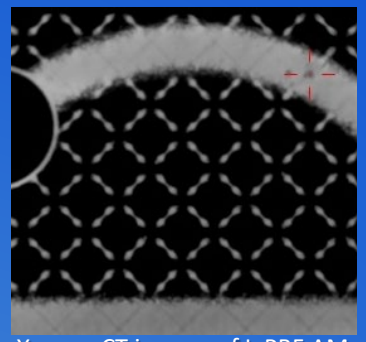
Laser Powder DED



L-PBF AM GRCop42 substrate with LP-DED HR-1 jacket.

Non-Destructive Evaluation Constraints

- X-ray CT and µ-CT
  - Unsuitable to high atomic number refractory metals
  - Elements with high radio-opacity (high scatter, low penetration depth) resulting in poor S/N and unresolvable images.
  - 225 kV, 450 kV, 2 MeV sources (MSFC).
- Linear Accelerator CT
  - 6 MeV x-ray: North Star Imaging
  - 6-7 MeV x-ray: RadiaBeam CAN.
  - C103 and W demonstrated. Mo in-work.
- Neutron Radiography / CT
  - Phoenix CAN in-review.
  - Potential for part activation (e.g. Hf in C103) impact transport, schedule, and handling.
  - National user facilities (e.g. DOE, NIST) not practical.
- Destructive Evaluation
  - Layer-wise imaging.
  - Control data.



X-ray µ-CT images of L-PBF AM AlSi10Mg part with build defect.

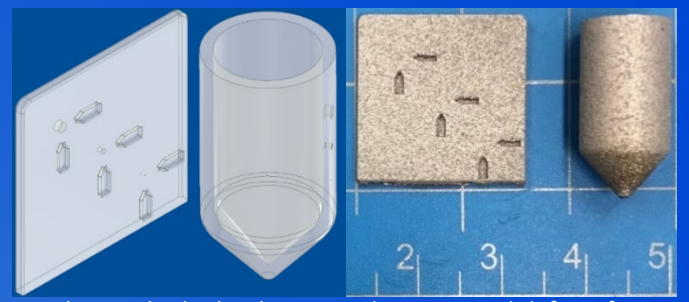
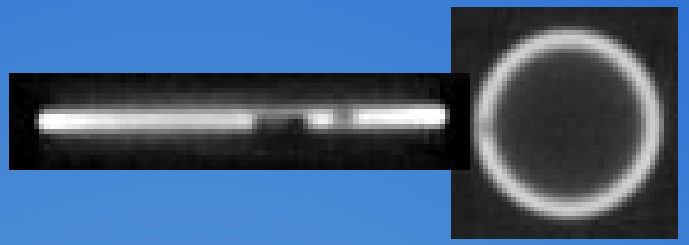
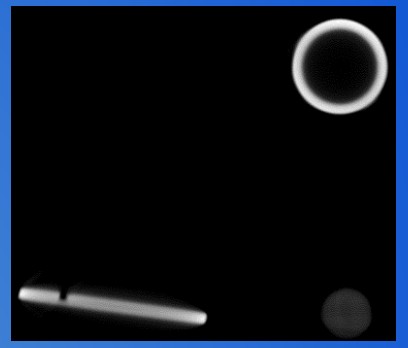


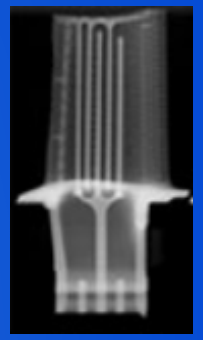
Plate and cylinder designs with engineered defects for NDE trials. AM W, Mo, and C103.



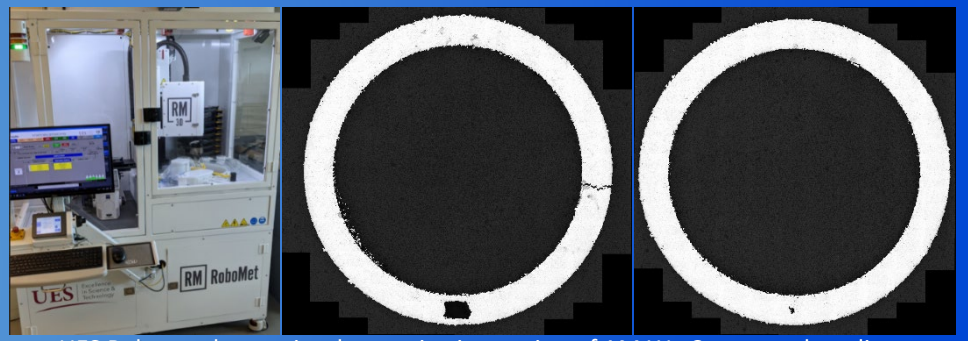
MSFC 2 MeV x-ray with 0.5 mm slice thickness of LPBF W. Course seeded defect resolvable.



RadiaBeam 7 MeV x-ray with 0.08 mm voxel of AM W and C103. Coarse and medium seeded defects resolvable.



Neutron-CT of Re turbine blade. Courtesy Phoenix.

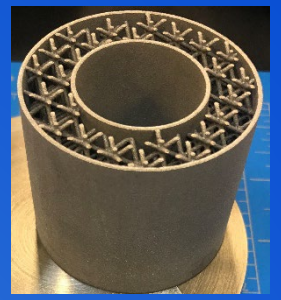


UES Robomet layer-wise destructive inspection of AM W. Coarse and medium flaws resolvable and determined fine flaw did not print.

Integration & Test

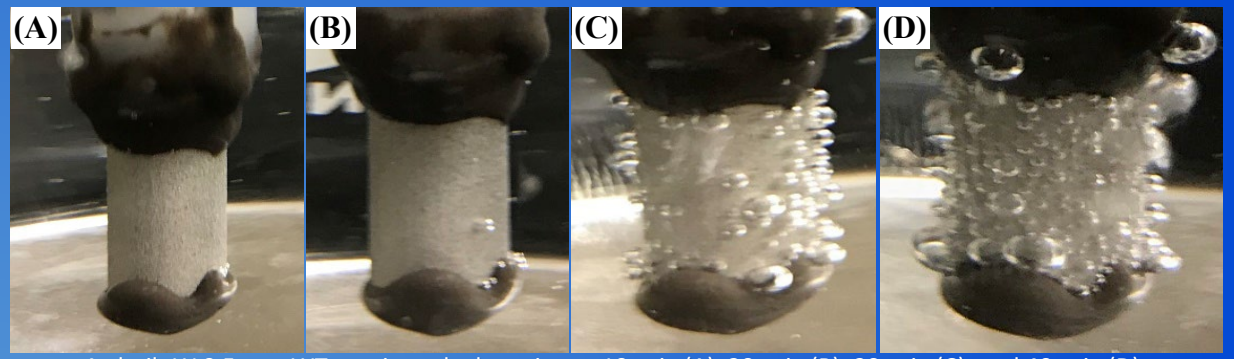
- Gas Permeability Tests
  - Impact of as-built microcracks and coatings.
  - 0.5 - 1.0 mm wall thickness.
  - Tested in the as-built condition.
  - Specimens were immersed in water and pressurized with N_2 in 10 psig increments to determine leakage.
  - All specimens experienced leakage at low pressure.

As-built L-PBF AM W leak test specimens with 0.5 mm WT.



L-PBF AM W SNP NTREES test section segment.

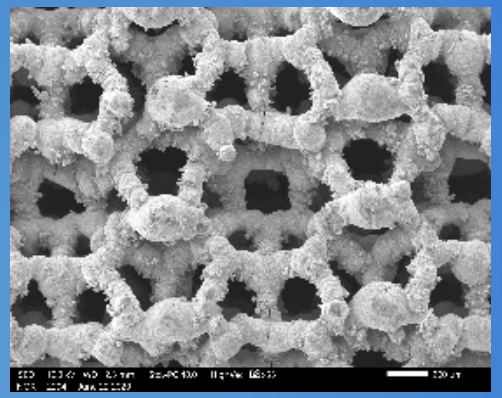
L-PBF AM W SNP CFEET Crucibles



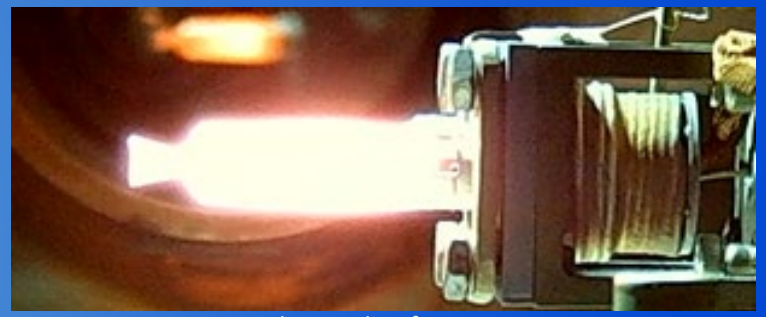
As-built W 0.5 mm WT specimen leak testing at 10 psig (A), 20 psig (B), 30 psig (C), and 40 psig (D).

- Demo Component Testing
  - Green propulsion vacuum chamber
  - CFEET
  - NTREES
  - INL TREAT reactor
  - CDA vacuum test
  - Nozzle extensions

L-PBF AM Mo 1 N reaction chamber and thrust stand-off.



Catalyst: ultra-fine lattice L-PBF AM W to be coated in Ir or print from Ir nano dispersoid.



Thruster hot-fire test.

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