

Additive Manufacture of Refractory Metals for Aerospace Applications

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Background

- Refractory metals and alloys are used for service in extreme high temperature environments:
 - Reaction Control System (RCS) thrusters.
 - Nuclear Thermal Propulsion (NTP) clad and structure.
 - Hypergolic / green propulsion chambers and catalyst.
 - Electric propulsion grids.
 - Power conversion system heat pipes.
 - 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 walled geometries (converging-diverging nozzles).
 - Relatively simple geometries.
 - High buy-to-fly ratio (20:1 to 50:1).
 - Low production rate.



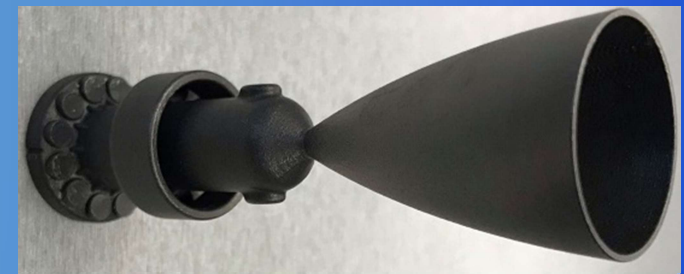
Apollo CSM RCS using C103. Courtesy Aerojet-Rocketdyne



Green propulsion Re thruster.



TZM Mo-alloy heat pipe. Courtesy Advanced Cooling Technologies.



Demonstration 5 N thruster made from Inconel 718 L-PBF AM.



Problem

- Traditional refractory manufacture is difficult and expensive:
 - Bar, plate, sheet stock limited (constrains design).
 - High feedstock cost.
 - Relatively difficult to form/machine (fracture prone).
 - Heat treatment requires specialized facilities (O, C, N sensitive).
 - Joining options limited.
 - Inspection options limited.
- Alloys designed for powder metallurgy (HIP, deposition), forging, and machining (EDM).
 - Re added to improve ductility (\$3.5k/kg).
- Feedstock vendors limited
 - Powder typically angular/unalloyed and does not meet AM specs.
 - Gas atomization methods limited by high T_m .

Base	Name	Composition
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 FS85	Nb-28Hf-13W-5Ti-2Ta-1Zr Nb-28Ta-10W-1Zr
Mo	Mo	Mo
	Mo-21Re	Mo-21Re
	Mo-41Re	Mo-41Re
	Mo-44Re	Mo-44Re
	Mo-47.5Re TZM	Mo-47.5Re Mo-0.5Ti-0.08-Zr-0.2C
W	W	W
	W-25Re	W-25Re
Ta	Ta	Ta
	Ta-10W	Ta-10W

Traditional Refractory Alloys

Alloy	T_m (°C)
AlSi10Mg	580
IN718	1247
IN625	1295
CoCrMg	1350
316L SS	1375
Ti6Al4V	1600
GRCo84	1750
C103	2350
Mo41Re	2428
Mo	2610
W25Re	3050
W	3410

AM Alloy Melt Temp

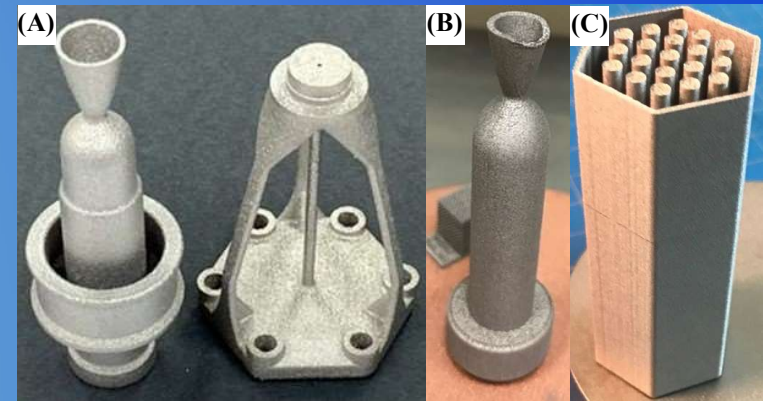
AM
SOA

Industry
Need



Methodology

- Refractory AM tech gap review / maturation path.
- Leverage AM to overcome traditional constraints.
 - Increased design freedom.
 - Higher feedstock utilization factor (decreased waste costs).
 - Eliminate / minimize joining.
 - Develop modern AM optimized refractory metal formulations.
- Refractory AM demonstrated using:
 - Laser powder bed fusion (L-PBF), electron beam PBF (EB-PBF), electron beam wire DED (EW-DED), and laser powder DED (LP-DED).
- Development Objectives
 - *Phase 1*: Use existing refractory metal powder.
 - *Phase 2*: Add dispersoids (e.g. ZrC or HfC ceramic nano-powder) to refractory metal powder.
 - *Phase 3*: Computation-based alloy design specifically for AM methods with emphasis on use of cost effective elements, printability, and properties (e.g. refractory high entropy alloys).



L-PBF AM (A) C103 1 N reaction chamber and thrust stand-off, (B) 1N tungsten chamber, W NTP fuel clad.



Powder Characterization & Optimization

- Refractory Metal Powder Production Options
 - Plasma spheroidization of angular powder (Nb, Ta, Mo, W, Re).
 - Plasma wire atomization (Nb-, Ta-, Mo-, W-base alloys).
 - Electrode Induction Gas Atomization (EIGA) of ingot (Nb-, Ta-, Mo-base alloys).

- AM Powder Specifications

- Alloyed elements
- Spherical morphology
- Fully dense particles (>99.9 %TD)
- Particle size distribution (PSD)

- AM Grade Powder Options

- Elemental: W, Mo, Ta, Nb.
- Alloyed: C103, Ta3W, T5W, Ta13W, FS85 (in dev).

- PSD

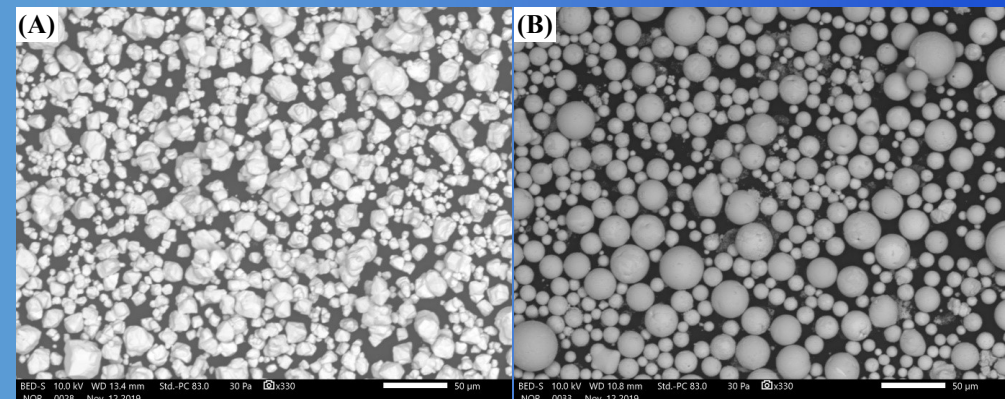
- L-PBF: 45-15 μm
- LP-DED: 63-150 μm



MSFC Tekna Tek15 plasma spheroidization of W powder.

Electrode Induction Gas Atomization of ingot. Courtesy Sandvik.

Plasma wire atomization. Courtesy GE AP&C.



Scanning electron micrographs of (A) as-received angular W powder and (B) RF plasma spheroidized W powder.



L-PBF AM Parameter Development

Parameters Development

- Energy predictions & experimental iterations.
- EOS M100: $\phi_l = 40 \mu\text{m}$

$$E_v = \frac{P}{vDt}$$

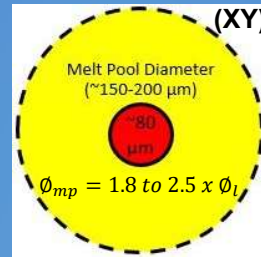
E_v = Volumetric Energy Density (J/mm^3)

P = Laser Power (W)

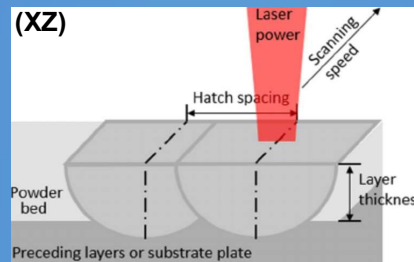
v = Laser Speed (mm/s)

D = Hatch spacing (mm)

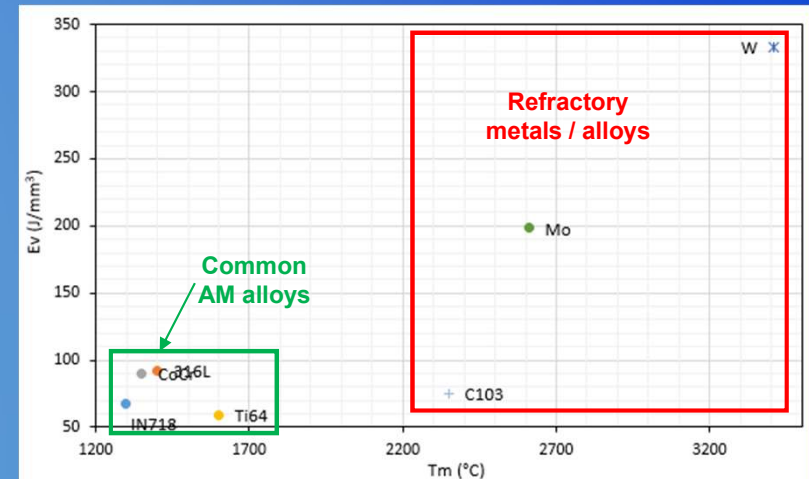
t = Layer thickness (mm)



L-PBF laser focus and melt pool.



L-PBF hatch spacing.



Melt Temperature vs. L-PBF energy density map.

Build Plate options

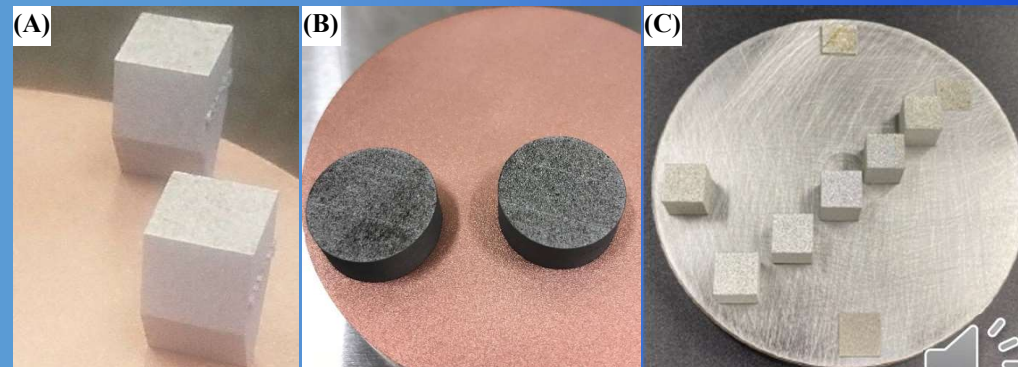
- W: 304 SS, W, CU110
- Mo: 304 SS, Mo, Ti6Al4V
- C103: Nb, C103.
- Ta: 304 SS, Ta.



MSFC EOS M100 printing W.

Process Gas

- High purity argon with very low O_2 and H_2O ($\sim 1 \text{ ppm}$).



L-PBF AM W metallographic (A), mechanical test (B), and Mo metallographic specimens (C).

Heat Treatment

- Stress Relief

- W: 1100-1200 °C for 1 hr in vacuum of 1×10^{-4} Torr.

- Hot Isostatic Press

- W: 1700-1800 °C from 172-193 MPa for 1-4 hrs ^[1]
- Ultra high purity argon.

- Recrystallization

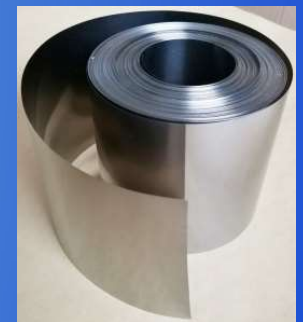
- W: 1250-1350 °C for 1 hr in vacuum of 1×10^{-4} Torr.

- Sacrificial Wrap

- O, N, C sensitive metals (e.g. Nb, Mo, Ta) must be foil wrapped during heat treatment.
- 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.



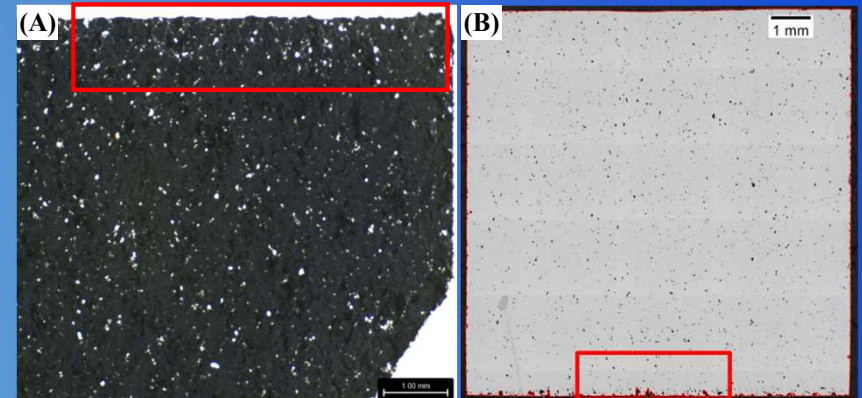
Ta foil for AM part wrap.



[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.

Characterization

- Optical Microscopy
- Density Measurements
 - Archimedes' method or He pycnometry
 - W 93-95 %RD
 - Mo 97.9 %RD
 - Typical L-PBF AM cutoff 99.5 %RD
- Tensile Testing (at 20 °C)
 - Psylotech meso-scale loadframe.
 - L-PBF AM is 50.7%UTS of wrought.
 - Micro-cracks have significant impact on mechanical properties.
 - High temperature mechanical test capability limited.

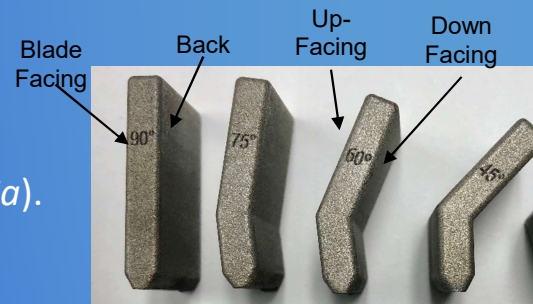


(A) Scanning electron micrograph of L-PBF as-built W and (B) optical micrograph of as-built Mo.

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	TBD
Wrought	349.26

- Surface Finish
 - Keyence VR-3200
 - Areal surface roughness (S_a).



As-Built L-PBF AM W Surface Finish Specimens

Surface Finish of As-Built L-PBF AM W

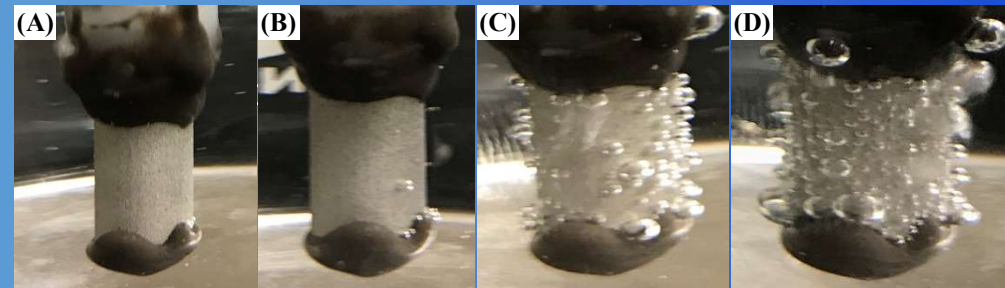
Condition	S_a (μm)								
	0° (vertical)		15°		30°		45°		90° (horiz)
	Blade-Facing	Back	Up-Facing	Down-Facing	Up-Facing	Down-Facing	Up-Facing	Down-Facing	Up-Facing
W As-built	5.5	6.3	5.4	7.3	6.1	8.9	9	15.7	

Leak Testing and Coatings

- W L-PBF AM parts have micro-cracks volumetrically distributed throughout the material
 - Characterize gas permeability
 - Propulsion applications requires some degree of gas retention.
- Leak Specimens
 - 0.5, 0.76, and 1.0 mm wall thickness.
 - Tested in the as-built condition.
 - Specimens were immersed in water and pressurized increments to determine leakage.
 - All specimens experienced leakage at low pressure.
 - HIP had no influence on leak behavior.
- Coatings and/or infiltration are potential near-term options until dispersoid or new AM alloys available.
 - Vacuum plasma spray, electro-deposition, LP-DED.
 - Same material as the AM substrate or compatible material.
 - Protective coatings normally required for refractory metals in oxygen service molybdenum-silicide or R512E (Si-20wt%Fe-20wt%Cr).



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

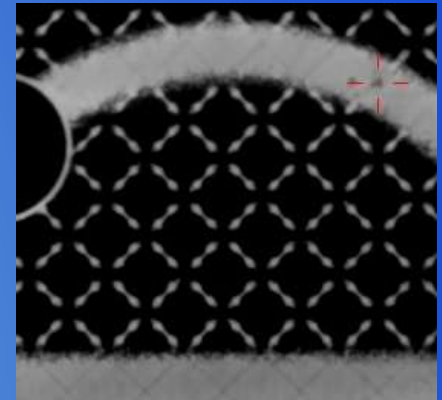


As-built W 0.5 mm WT specimen leak testing at 10 psig (A), 20 psig (B), 30 psig (C), and 40 psig (D).

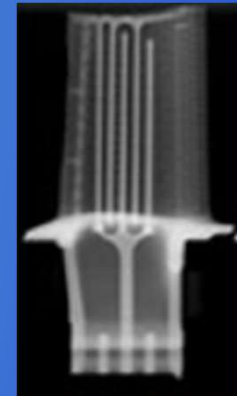


Non-Destructive Evaluation Limitations

- X-ray computer tomography (CT) and micro-focus CT (μ -CT)
 - Relied on heavily for inspection of complex AM parts.
 - Unsuitable for refractory metals due to high radio-opacity resulting in high scatter, low penetration depth, and poor signal-to-noise ratio equal unresolvable images.
- Neutron CT
 - Limited commercial vendors.
 - Potential for part activation to impact schedule and handling.
 - National user facilities (e.g. spallation neutron source) not practical since emphasis is R&D not meant for serial inspection.
- Ultrasonic Testing
 - Difficult for AM due to the inherently rough surface finish.
 - Requires surface enhancement for use.
 - Surface finish occurs after inspection and increases cost/schedule.



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



Neutron-CT of turbine blade.
Courtesy Phoenix.



Conclusions

- Conclusions

- Refractory metal AM been demonstrated as viable with W, Mo, Ta, C103, as well as several refractory alloys in development.
- Substantial alloy, feedstock, AM method, and post-processing development is required to optimize refractory metal AM to the broad array of aerospace applications.

- Recommendations for future work

- Continued development of dispersoid strengthened refractory metals, new solid solution and refractory high entropy alloys.
- Expansion of refractory AM feedstock options and suppliers.
- Heat treatment schedule optimization for existing and new material options.
- Surface finish enhancement evaluations.
- Specialized NDE methods applicability requires evaluation.
- Coating process, material options, and adherence evaluations required.
- Elevated temperature mechanical testing (inert or vacuum) requires commercial expansion.
- Component hot fire testing to build TRL of refractory metal AM.



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