Materials Evaluation of Additively Manufactured Fuel Injector Candidates

NATIONAL
ENERGY
TECHNOLOGY
LABORATORY

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In partnership with Siemens

Anand Kulkarni

Ramesh Subramanian

University Turbines Systems Research

2023 Project Review Meeting

Solutions for Today | Options for Tomorrow

U.S. DEPARTMENT OF ENERGY

Disclaimer

Acknowledgements

- *NETL Advanced Turbines Program under FWP-1022408 (EY21, EY22, EY23, …)*
- *Siemens Energy – AM Solutions for L-PBF additive manufacturing and heat treatment*

- *Pete Strakey for injector face temperature modeling*
- *Dustin Crandall for CT analysis*
- *Ömer Doğan and Kaimiao Liu for useful discussions*
- *Chris Powell & Devin Hlvanika for mechanical testing*
- *Dennis Harvey & Matthew Fortner for metallographic preparation*
- *Trevor Godell for test bar machining*

Outline

Materials Evaluation of Additively Manufactured Fuel Injector Candidates

- **About NETL Alloy and AM Research**

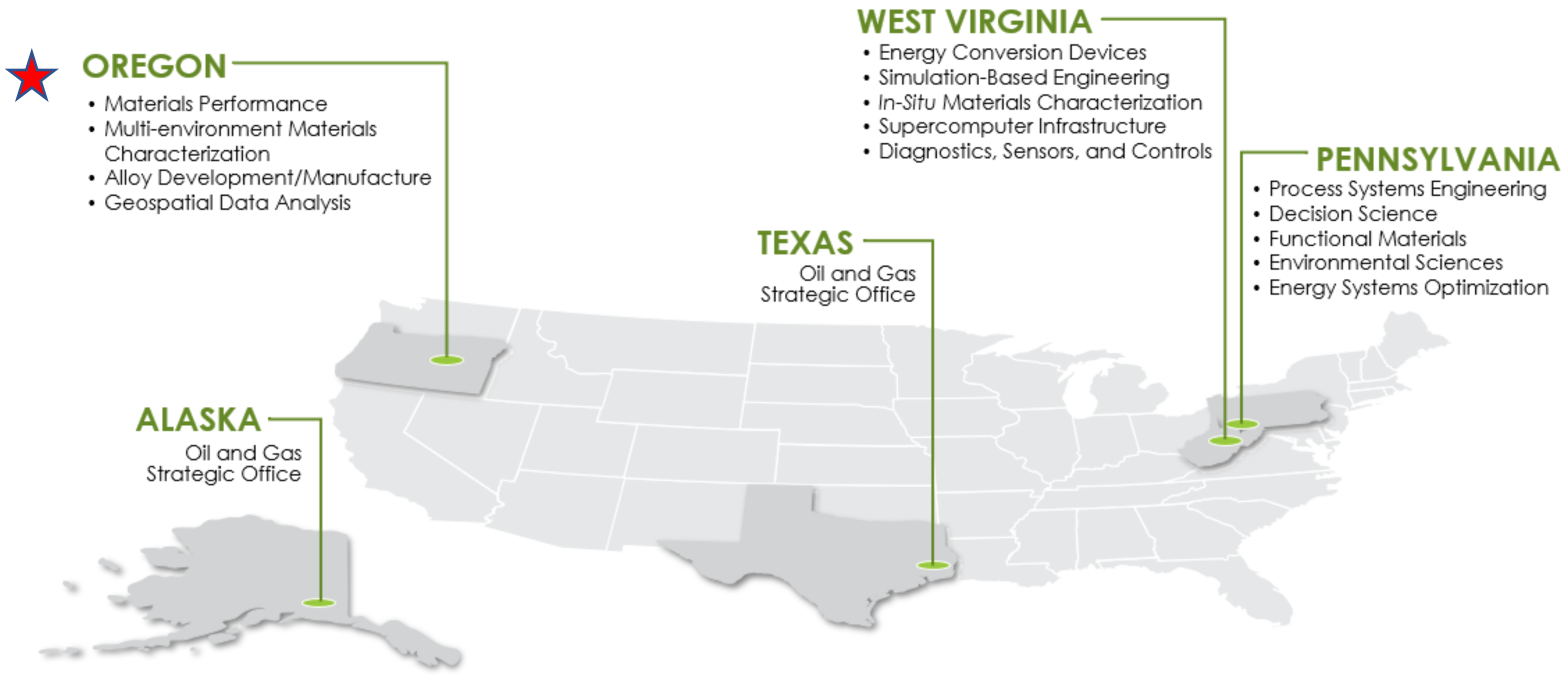
- **Project Overview**
- **Results on Injector Candidate 1 – IN 625**
  - Microstructure, Tensile, and Creep
- **Select results on All Candidates**
  - Location-specific grain structure, 750°C Oxidation, Hydrogen Embrittlement Screening

- **Summary & Concluding Remarks**

National Energy Technology Laboratory (NETL)

One of 17 U.S. Department of Energy (DOE) national laboratories; producing technological solutions to America's energy challenges.

Multiple Sites Operating as 1 LAB System



OREGON
- Materials Performance
- Multi-environment Materials Characterization
- Alloy Development/Manufacture
- Geospatial Data Analysis

WEST VIRGINIA
- Energy Conversion Devices
- Simulation-Based Engineering
- *In-Situ* Materials Characterization
- Supercomputer Infrastructure
- Diagnostics, Sensors, and Controls

TEXAS
Oil and Gas Strategic Office

PENNSYLVANIA
- Process Systems Engineering
- Decision Science
- Functional Materials
- Environmental Sciences
- Energy Systems Optimization

ALASKA
Oil and Gas Strategic Office

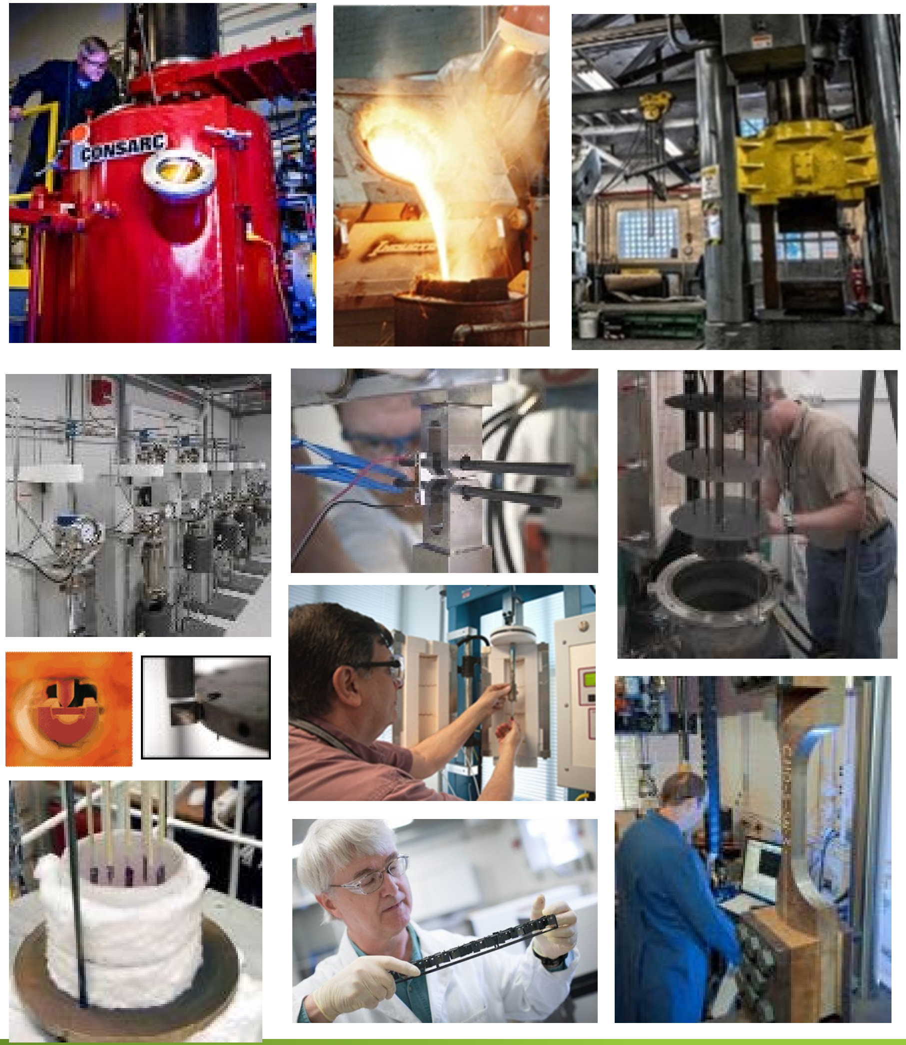
- NETL has three research sites
- Two strategic office locations
- **Unique within DOE:** Government owned & operated
- Research & Innovation Center world-class applied R&D (internal)
  - Diverse Partnerships Paths
- Technology Development Center federally sponsored R&D (external)
  - RIC technical POC
- **Only National Lab solely dedicated to carbon management research**

PI has been with NETL for 3 years & involved in metal AM since 2012

- **NETL RIC is building up internal and collaborative project work in metal AM**
- **NETL TDC has a range of funded projects across its portfolio in metal AM**

NETL Alloy Processing, Characterization, and Testing Capabilities

Structural Materials in Harsh Environments
Computationally Guided Alloy Design



Melt Processing - Scales translate to industrial practice

- Air Induction Melting up to 300 lbs; VIM: 15, 50 and 500 lbs
- Vacuum Arc Remelt/Electro-Slag Remelt 3-to-8-inch diameter ingots
- Directional Solidification VIM 200lbs; EB Furnace; Optical Float Furnace

Thermo-Mechanical Processing

- 500 Ton Press Forge; Roll mills: 2 and 4 high configurations.
- 900 Ton Extrusion Press (3Q CY24); Wire drawing equipment (2Q CY24)

This materials evaluation utilizes a range of capabilities

★ **NETL Severe Environment Corrosion Erosion Research Facility (SECERF)**

- Max temps: 1600°C; Erosion rig: 750°C; Gases: CO, CO_2, CH_4, H_2, H_2S, SO_2, HCl, O_2, N_2, He, air, H_2O vapor; Mixtures with mass flow controllers at 5-1600 ml/min

★ **Microstructural (SEM, TEM, EPMA, XRD, CT) and Chemical Analysis (XRF, LECO)**

Corrosion, Oxidation, and Heat Treatment Processing

- ★ *Heat-treatment furnaces:1650°C, inert atmospheres & controlled cooling*
- *Steam Autoclave:* Dual rated at 760°C / 310 bar and 746°C / 345 bar
- *Supercritical CO_2 Autoclave:* rated at 800°C / 275bar
- Static & Flow Through Autoclaves: CO_2 O_2, SO_2, H_2S Up to 5000psi & 500°C

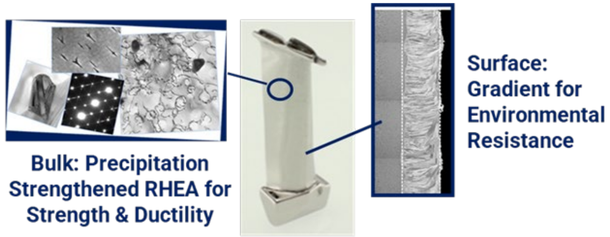
Fracture Mechanics and Creep Laboratories

- ★ Tensile, fatigue and creep testing up to 1000°C in air. Screw driven & servo-hydraulic frames (max. load 1000 kN). Constant stress & strain load frames
- ★ Mechanical testing in H_2 and CO_2 at high gas pressure (up to 5000 psi and 250°C and electrochemical H_2 charging (on-line in CY 2023).

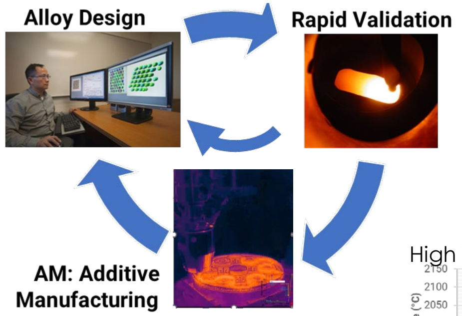
NETL RIC Additive Manufacturing (AM) Research

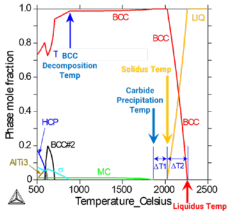
Refractory High Entropy Alloys Designed For AM

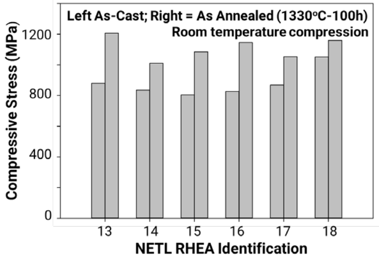
★ NETL Led, partners ORNL and CMU



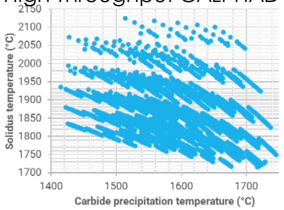
Images of representative precipitation strengthened alloy and gradient surface

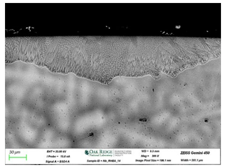






High Throughput CALPHAD





Affordable, Durable
> 1300°C Turbine Alloys

Solid Feedstock Development

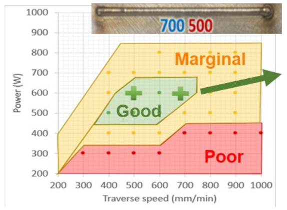
Wire Arc Additive Manufacturing (WAAM). Cost-effective manufacturing of components

- ★ High deposition rates (up to 5 kg/h) with large build envelope
- ★ Potential to reduce production times & material scrap
- ★ Wire feedstock cost can be significantly lower than powder
- ★ Expanding NETL capabilities to produce custom wire feedstocks
- ★ ICME approach to design alloys for WAAM and other solid feedstock additive and advanced manufacturing methods.

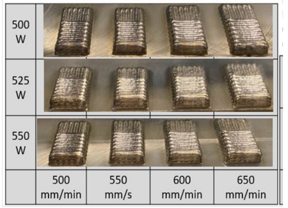
Optimizing Laser Wire-Direct Energy Deposition (LW-DED) of Alloy Haynes 282

- ★ Partners: Haynes, Oregon State University

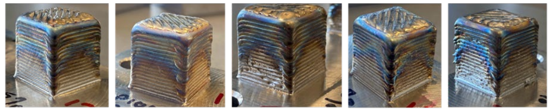
Quality Map – Single-bead tracks



Short Stacks



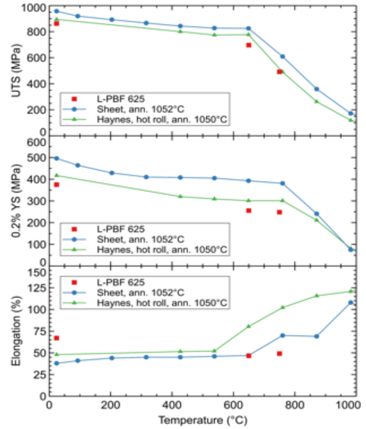
Robust and consistent printing with larger wire



Enable High Deposition Rate Additive & Hybrid Manufacturing

Impact of H_2 on AM Components for Hydrogen Turbines

- ★ Additive manufacturing (AM) techniques increasingly used to produce components, such as fuel injectors, for turbines.
- ★ Hydrogen damage is sensitive to microstructure which develops during manufacturing.
- ★ AM processing can lead to grain elongation, grain boundary segregation - less than optimal structure to resist hydrogen
- ★ Novel processing strategies, heat-treatments, and custom feedstocks to enhance H_2 resistance



Tensile properties of IN625 produced by **Laser-powder bed fusion (L-PBF)** AM compared to conventional IN625. Testing at NETL.

Examine & Improve Hydrogen Resistance of AM Superalloys-

Design, Application & Optimization for Turbines

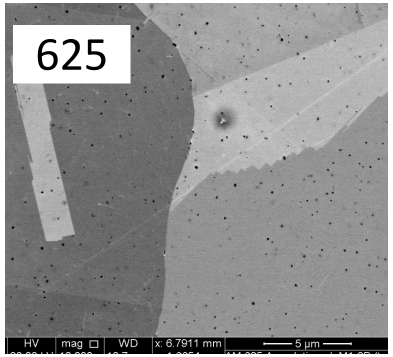
Enable Advanced Design in Next Generation Engines

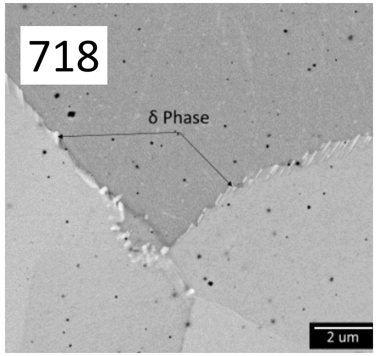
Collaborations & University Partners

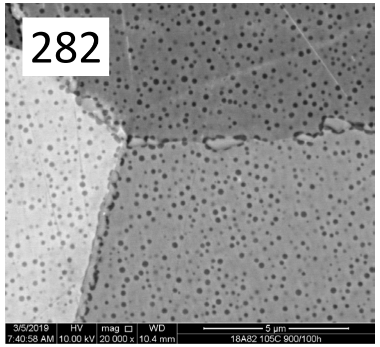
SIEMENS
HAYNES International
OAK RIDGE National Laboratory
OMIC R&D Collaborate. Innovate. Elevate.
Oregon State University
ATAMI
University of Pittsburgh
Carnegie Mellon University
West Virginia University

Materials Evaluation of Additively Manufactured Fuel Injector Candidates

L-PBF 625, 718, and 282



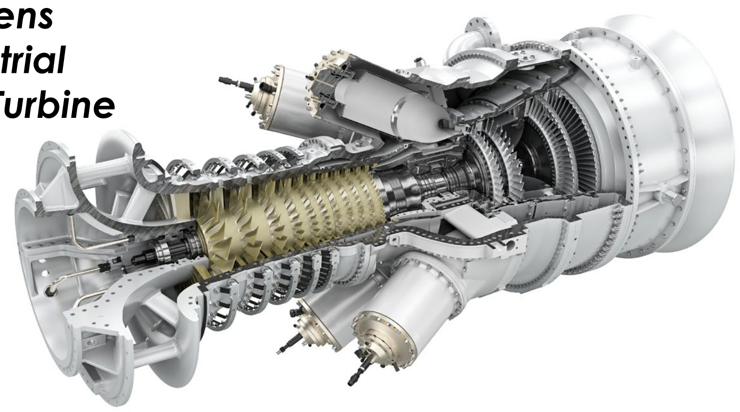


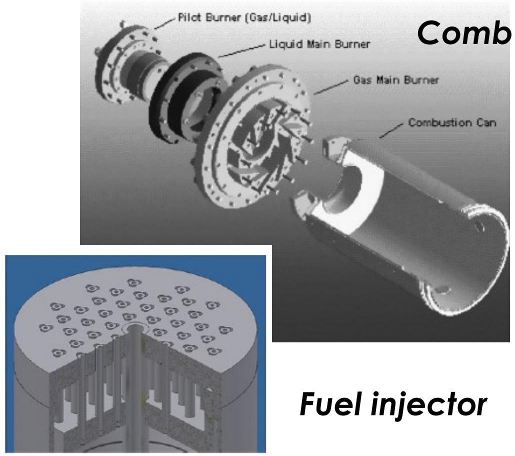


Motivation - AM micro-mixing injectors for hydrogen combustion

- **Hydrogen turbine technology**: Hydrogen fuel and hydrogen/natural gas blends are being pursued for potential to reduce emissions and improve engine operating efficiency
- **Laser powder bed fusion (L-PBF) fabrication**: Design of fuel injectors with cooling passages & fuel channels for both premixed and non-premixed gas turbine combustion systems

Siemens Industrial Gas Turbine





Combustor Can

Fuel injector

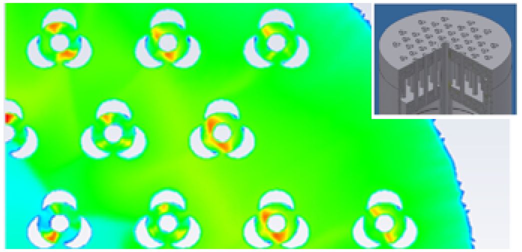
AM Micro-mixing injectors development by OEMs

OEMs using AM to fabricate combustor parts

Parallel & separate in-house modeling effort (FEA, CFD), bench-scale testing & select swirler design

Max Operation Threshold Targets

650°C 750°C 815°C



Injector Face - Micro swirlers (NETL - P Strakey)

NETL-MGN Modeling predictions

Max Avg. Face Temp : 400 – 700°C with localized hot spots

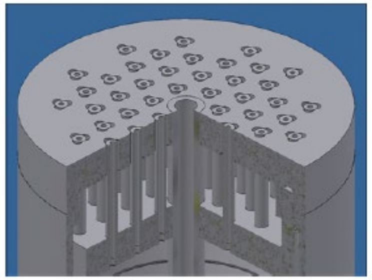
Worst case, No injector cooling ~ 1000°C Avg. Max Temp

Ni-based superalloys used due to service demands

GOAL: Materials evaluation of L-PBF superalloys fuel injector candidates for hydrogen service → Down selection

Materials Evaluation of Additively Manufactured Fuel Injector Candidates: IN625, IN718, H282 Ni superalloys

Hydrogen behaves very differently from natural gas in terms of flame-speed, mixing, molecular diffusion and materials compatibility



650°C | 750°C | 815°C

Project Directions:

- Engage Siemens in L-PBF printing, heat treatment, & feedback on materials study
- Screen the tensile, creep, and fatigue properties up to 815°C in air and compare with conventionally processed alloys
  - ➢ Porosity / defects - Location specific microstructure – Impact of minor phases
  - ➢ Failure mechanisms
- Examine the effect of surface conditions on the 750°C isothermal oxidation behavior
  - ➢ Machined vs Printed Surfaces (Exterior vs Interior Passages)
- Assess hydrogen embrittlement susceptibility using slow strain-rate tensile testing
  - ➢ Ex-situ electrochemically charged and then test to failure
  - ➢ Extend to in-situ testing, examine elevate temperature hydrogen attack and damage
- Screen materials behavior under conditions that mimic service
  - Coupon exposure various fuel environments at elevated temperature, pressure, and H2O vapor
  - Capture prior thermal history& assess impact on select properties

Invest in H_2 Testing

Future Work

Approach to baseline microstructure & property evaluation

Injector Alloy Candidates: IN625, IN718, Haynes 282

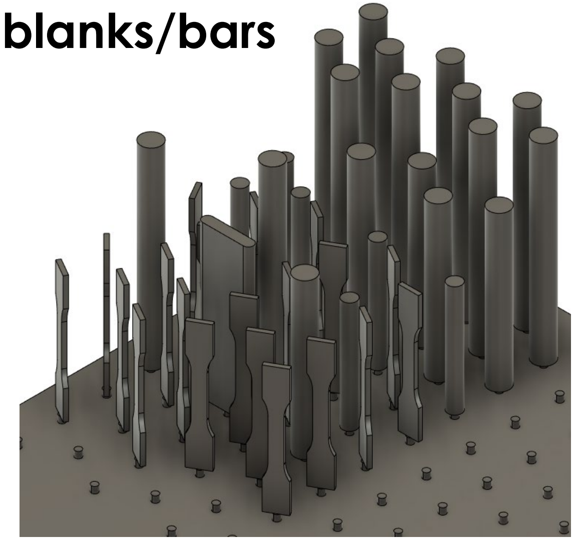
FOCUS: Processing-Structure-Property Relationships; Compare to Wrought; Failure Mechanisms; Hydrogen Degradation; Service-Like Conditions

L-PBF Additive Manufacturing at Siemens Energy – AM Solutions

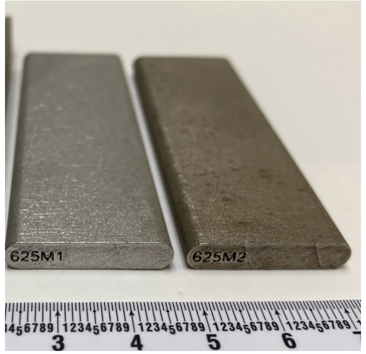
EOS M290 machine using optimized parameters (40 µm layer thickness)

Specimens in the build direction (Z), Stress Relieved, and then Heat treated to standard commercial specifications

42 blanks/bars



Met Bar 1 (as-printed)
Met Bar 2 (solutioned)



(5) Tensile / Creep Z-blanks

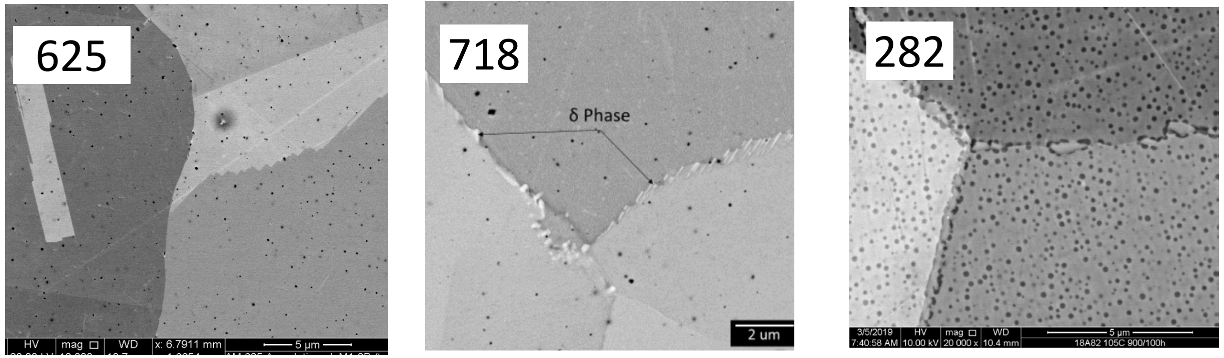
(13) Oversized Z-blanks

(20) Z-dogbones HE Tests

Materials and Approach

Superalloys 625, 718, 282 - balance of fabricability, durability, & environmental resistance

Solid Solution vs. γ'/γ"/δ Precipitate vs. γ' Precipitate Strengthened



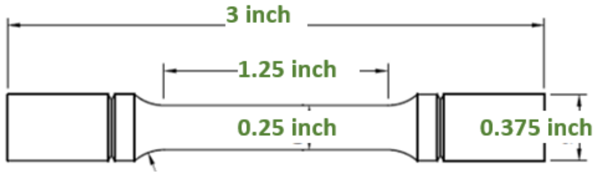
Stress-relieved & Fully-heat treated L-PBF alloys 625, 718, 282

- **Tensile tests (E8/E21) at Room Temp, 650°C, 750°C**
  - 1 test each at 2.17x 10^{-3} mm/s to1.2%, then 2.17 x 10^{-2} mm/s
- **Creep rupture tests (E139)** Various conditions at 650 – 815 °C / 100 – 600 MPa
- **Strain-controlled low cycle-fatigue at 650 °C**
  - Strain-to-failure vs Fatigue Life curve (S-N curve)
  - R= 0.05, f= 0.2 Hz for strain range up to 1.2%
- **Hydrogen embrittlement – Slow strain tensile tests at RT**
  - Faces are surface milled, then hand-polished with 600 grit paper
  - Single test for as-received, Triplicate testing for charged condition
  - Ex-situ H_2 charging at 1mA/cm2 in 0.1 M H_2SO_4 with +1 g/L CH_4N_2S for 72 h
  - Test to failure using **6.3 x 10^{-6} s^{-1}** strain rate

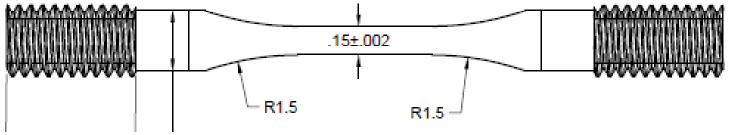
XRF/LECO Measured Compositions

Wt.%	Ni	Cr	Mo	Nb	Fe	Ti	Al	Co	C
L-PBF 625	61.5	21.3	9.1	3.7	4.0	0.08	0.06	0.08	0.0124
L-PBF 718	52.9	18.7	3.1	5.16	18.3	0.96	0.48	0.21	0.0525
L-PBF H282	58.1	19.2	8.8	0.05	0.11	2.12	1.22	10.3	0.0459

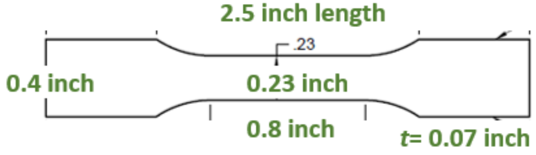
Tensile & Creep Test Bars (Same Geometry)



Low-Cycle Fatigue (8 bars) + 3 Spare blanks



Near-net shape HE Dogbones (4-5 bars per condition)



- **In-situ H2 tests**
- **Ex-situ H2 tests - Service exposure**

Background – Injector Candidate 1

Alloy 625

Nominal	Ni	Cr	Mo	Nb	Fe	C	Si	Mn	Ti	Al	Co
(wt.%)	Bal	21-23	8-10	3.15-4.15	≤ 5	≤ 0.10	0.5	0.5	0.4	0.4	1

- Solutioned-strengthened by Mo, Nb
- **Stress relieved on build plate then solutioned at 1175°C for 1 hour (No HIP)**
- Primary Nb-rich MC carbides dispersed throughout; Secondary Cr, Mo-rich carbides at the grain boundaries ($M_{23}C_6 + M_6C$) → ***dissolution to TCP*** ($\sigma + \mu$)
- MC carbides stable to 1100°C+; Al_2O_3 and TiN inclusions stable above liquidus
- Somewhat age hardenable w/**Ni_3Nb ppts 649-871°C** : **Metastable γ" → δ**

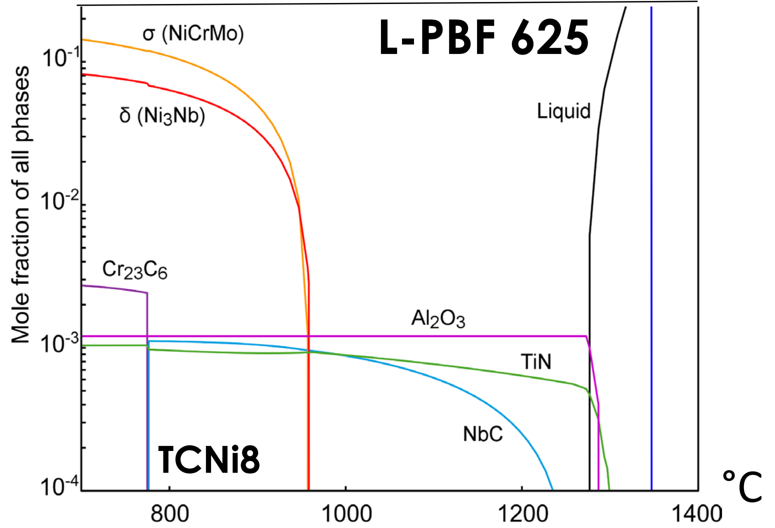
Max Operation Threshold Targets based on modeling predictions

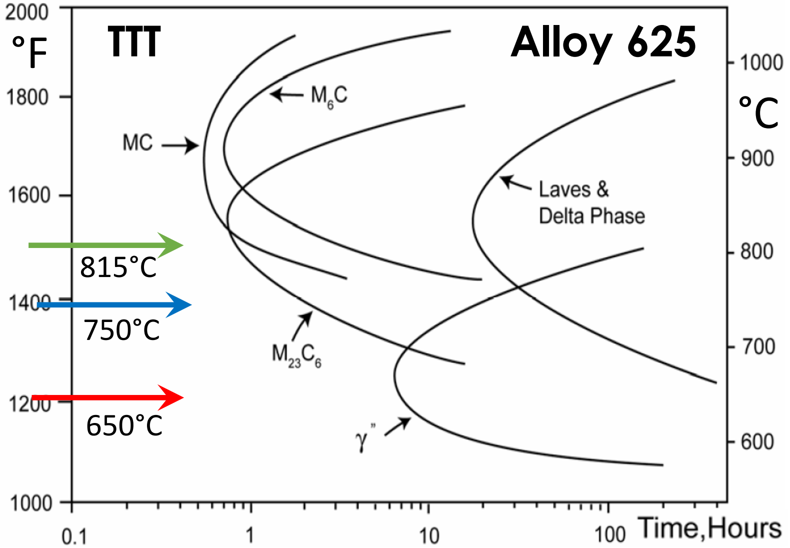
815°C

750°C

650°C

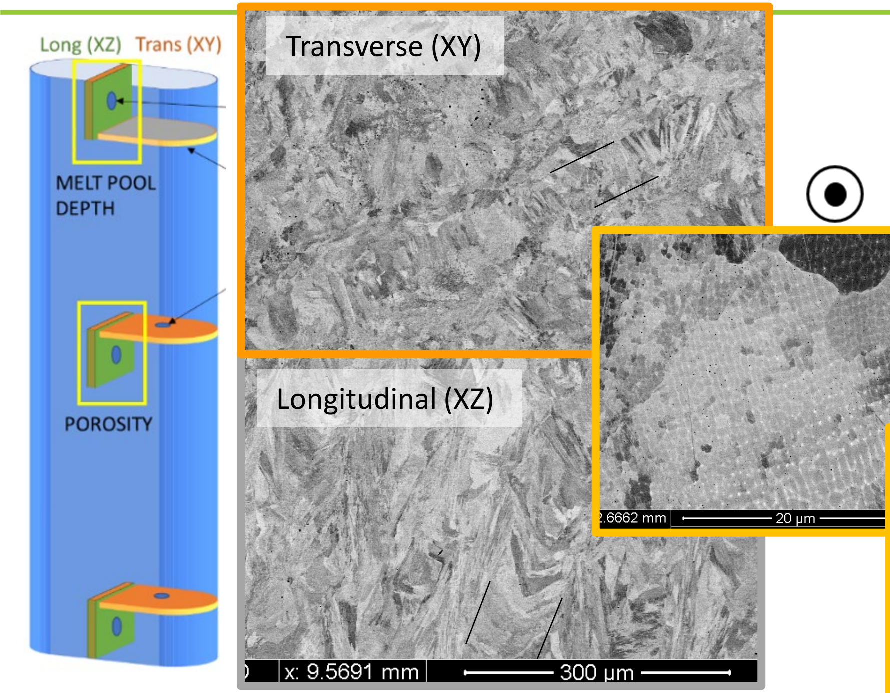
Phase Diagram

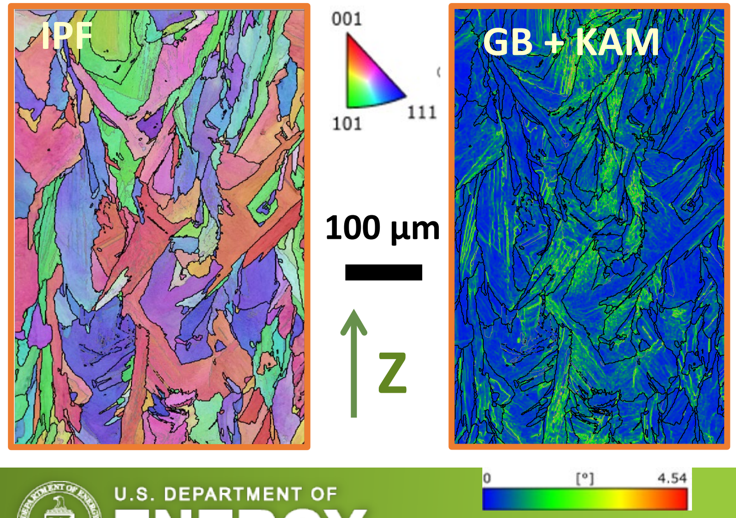




Shoemaker, Superalloys 718, 625, 706 (2005) 409

As-printed L-625 microstructure (EOS M290, 40 µm MLT)



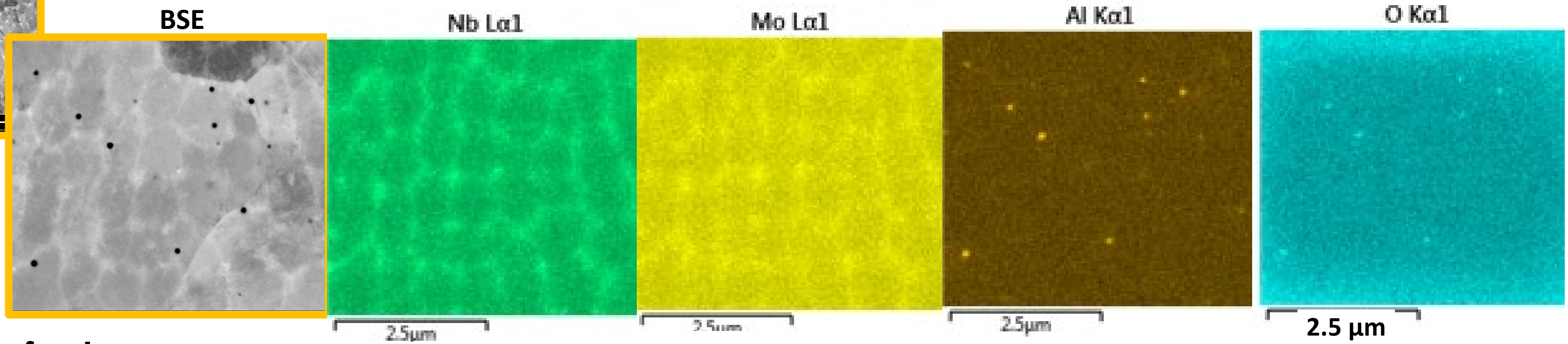


Composition of L-PBF 625 from XRF and LECO (wt.%)

	Ni	Cr	Mo	Nb	Fe	C	Si	Mn	Ti	Al	Co
(Max)	Bal.	23.0	10.0	4.15	5.0	0.10	0.50	0.50	0.40	0.40	1.0
(Min)		20.0	8.0	3.15	-	-	-	-	-	-	-
L-PBF 625	Bal.	21.3	9.1	3.7	4.0	0.0124	**0.04**	**0.04**	**0.08**	**0.06**	**0.08**

***C: 124 ppm*, N: 119 ppm, O: 194 ppm, S: 20 ppm by LECO**

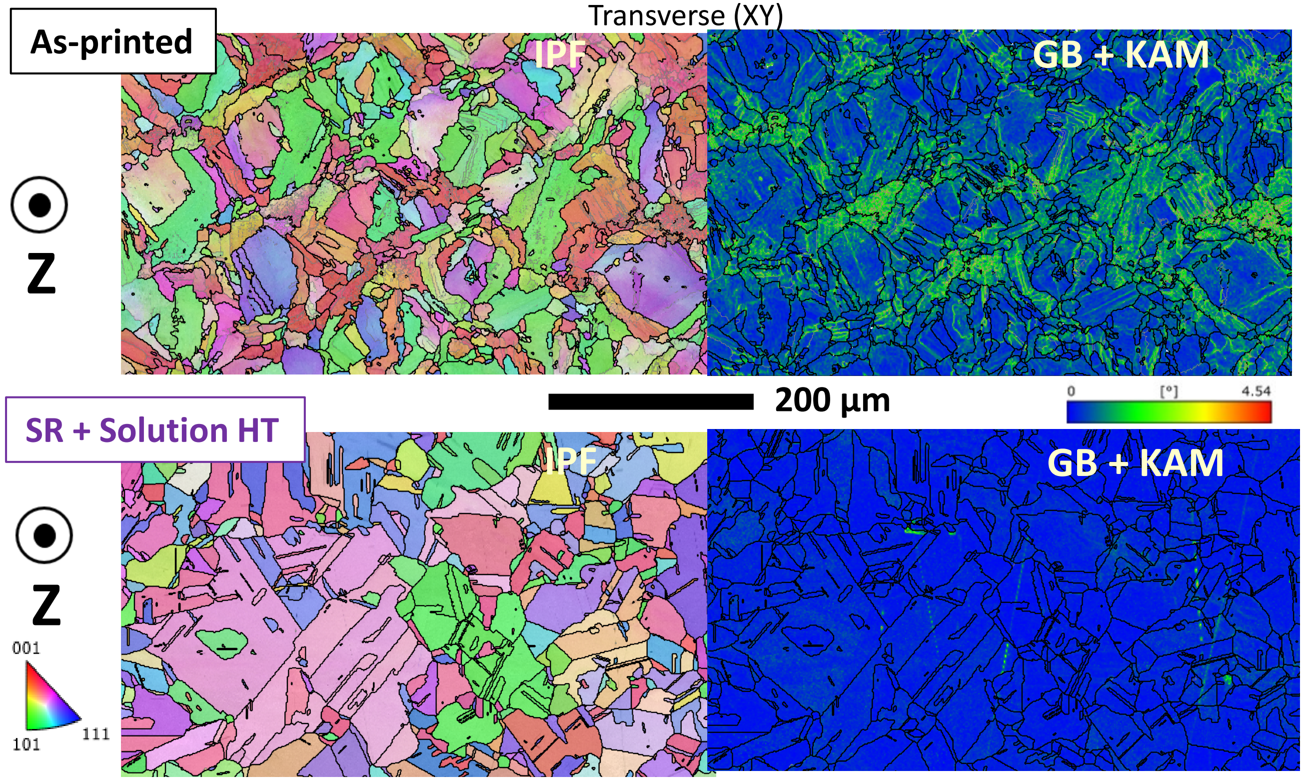
Low carbon content

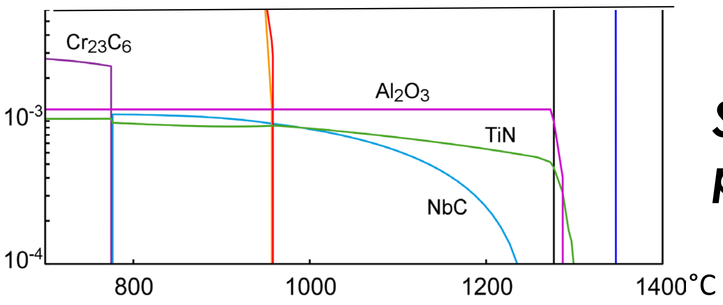


Key features:

- Highly dense (0.04 ± 0.02 % porosity), **appears that HIP is not necessary**
- Dendritic cellular structure with refractory elements at cell boundaries
- Turbulent, scalloped & weaved grains with deep melt pools (177 ± 15 µm) with accumulated strain
- Distribution of fine sub-micron **Al_2O_3 (and Ti-based) inclusions, possibly from thin oxide on AM powder surfaces → Highly stable! Likely no ODS effect**

As-solutioned L-PBF 625 microstructure

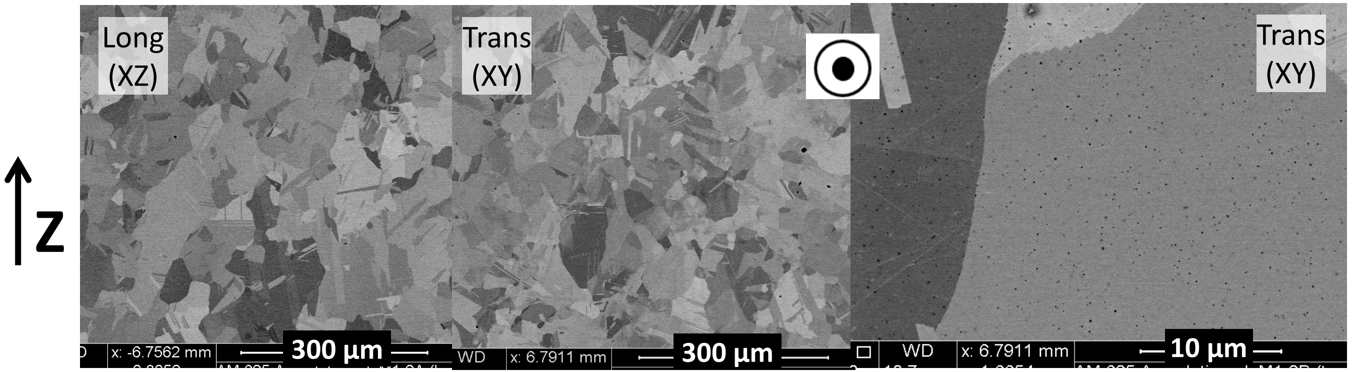


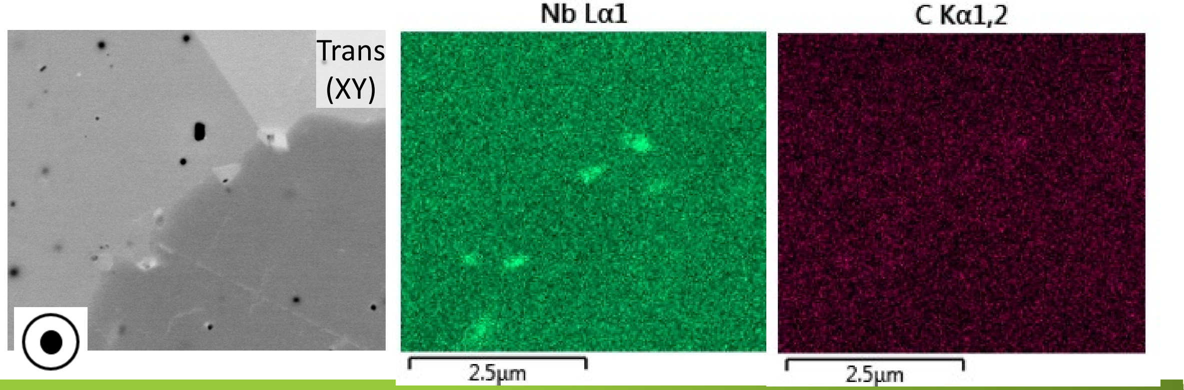


Solutioning in single phase region

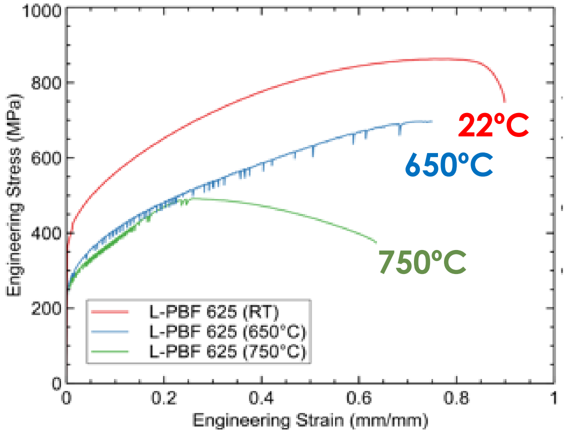
Stress relieved then solutioned at 1175°C for 1 hour (No HIP)

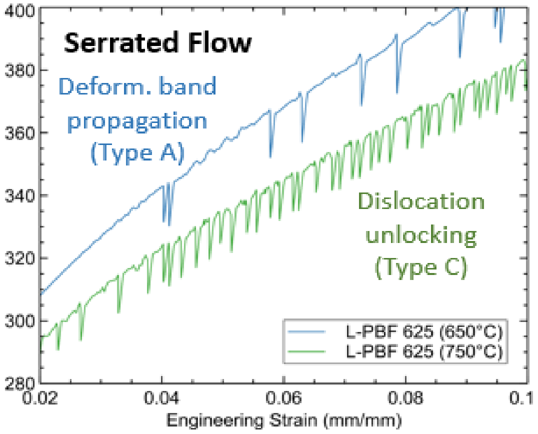
- Residual stress for L-PBF fabrication is fully relieved
- Fully recrystallized, equiaxed grains (Avg GS = ~60 µm) → isotropic properties
- ***MC carbides are micron-sized & distributed sparsely at GBs***: The carbon content at 124 ppm is 8 times below maximum threshold specified and is low
- Fine distribution of Al_2O_3 inclusions is stable



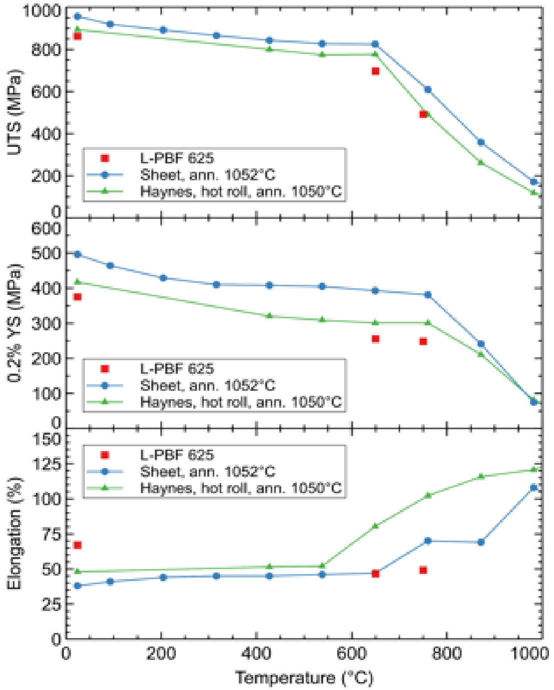


Fast Tensile Behavior of As-Solutioned L-PBF 625

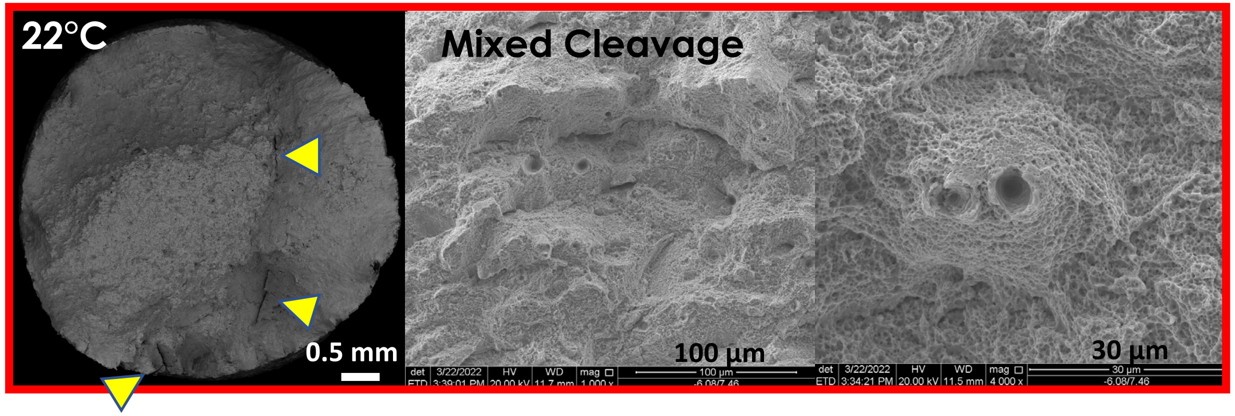


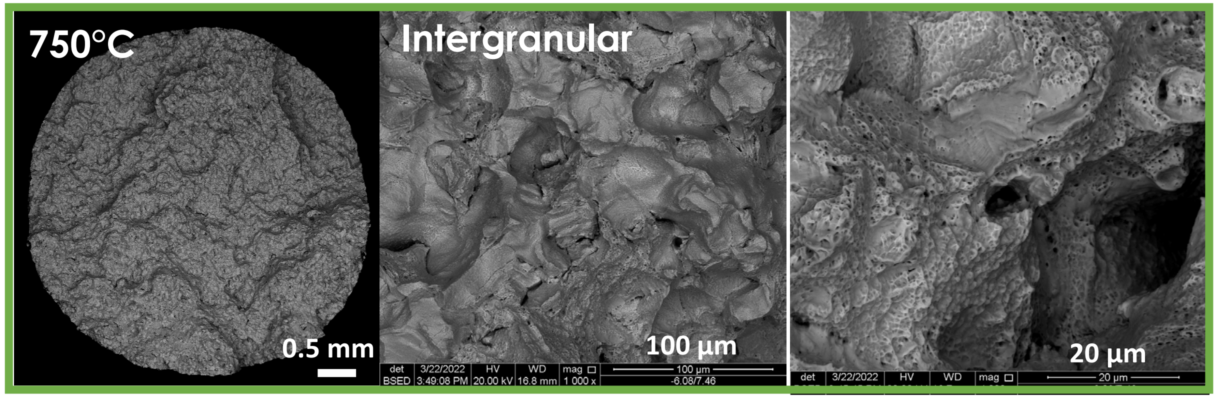


Alloy	Temp. (°C)	UTS (MPa)	0.2% YS (MPa)	Elongation (%)
L-PBF 625 Fully heat treated	RT	862	375	67
	650 (broke at indent)	697	256	(47)
	750	492	248	49



- Comparable properties to conventional 625, sheet material with refined grain structure so higher UTS and yield strength expected
- Serrated flow when tested at 650°C and 750°C
- Fracture surfaces show typical ductile dimpling and void coalescence

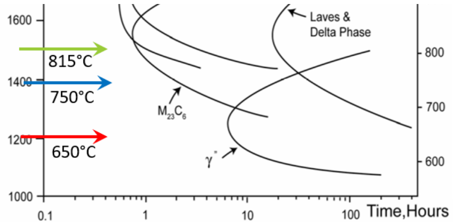


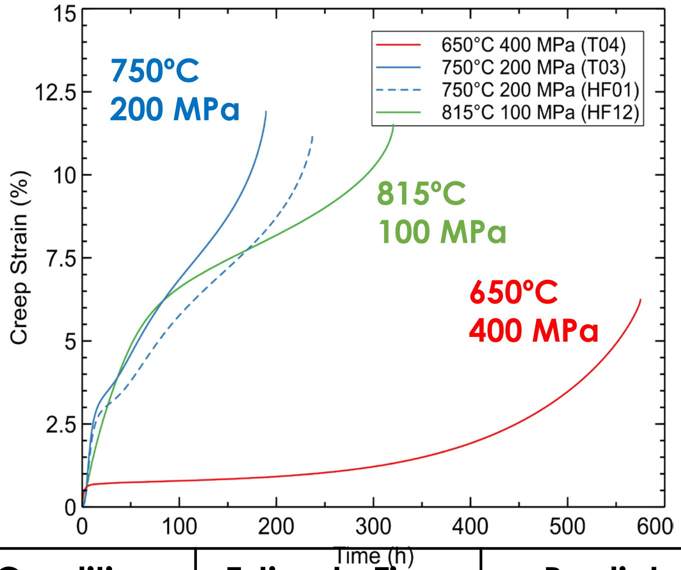


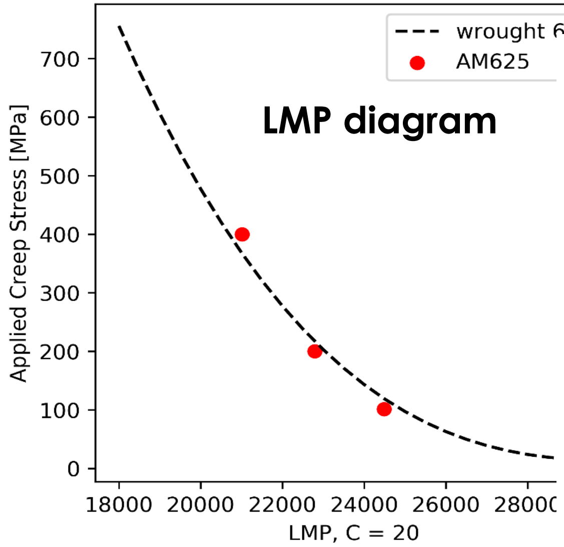
High temperature creep behavior of As-solutioned L-PBF 625

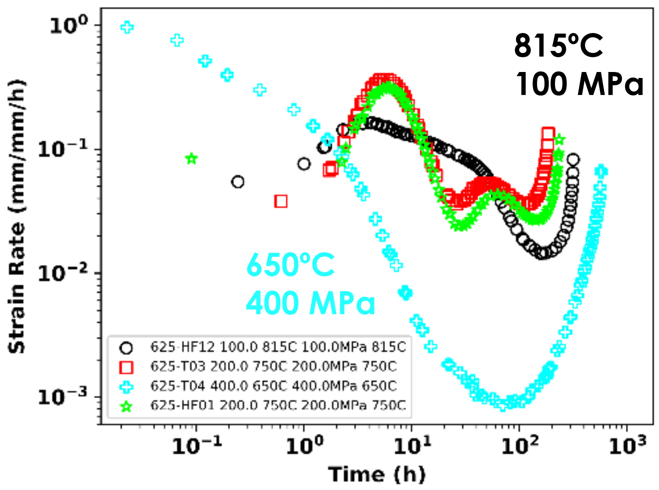
For hold temperatures

650°C –815°C







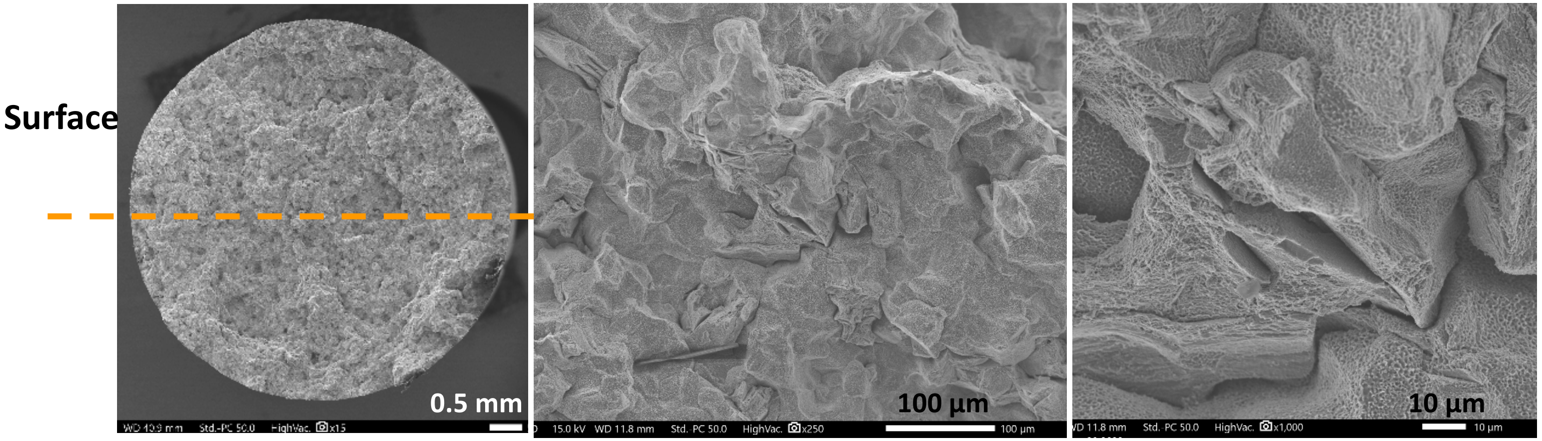


Alloy	Testing Condition	Estimate Time to failure	Predicted LMP (C=20)	Actual Time to failure (h)	LMP (C=20)	Elongation to Failure (%)	Min. Creep Rate (%/h)
SR + As-solutioned L-PBF 625	650°C @ 400 MPa	732	21107	**575**	**21011**	10.5	0.00086
	750°C @ 200 MPa	131	22630	**189**	**22792**	9.6	0.035645
	750°C @ 200 MPa	(repeat)	(repeat)	**237**	**22893**	8.3	0.02405
	815°C @ 100 MPa	222	25098	**320**	**24489**	9.9	0.014439

- **Performs like wrought! Larson-Miller parameter diagram shows creep rupture lives for As-Sol. L-PBF 625 consistent with wrought 625**
- **Similar creep ductility for these applied loads over the temperature range (E= 8.3 – 10.5 %)**
- **750C at 200 MPa (Tf= ~200 h): Multiple creep rate minima likely relates to emergence of γ” first, then δ → TEM analysis underway**

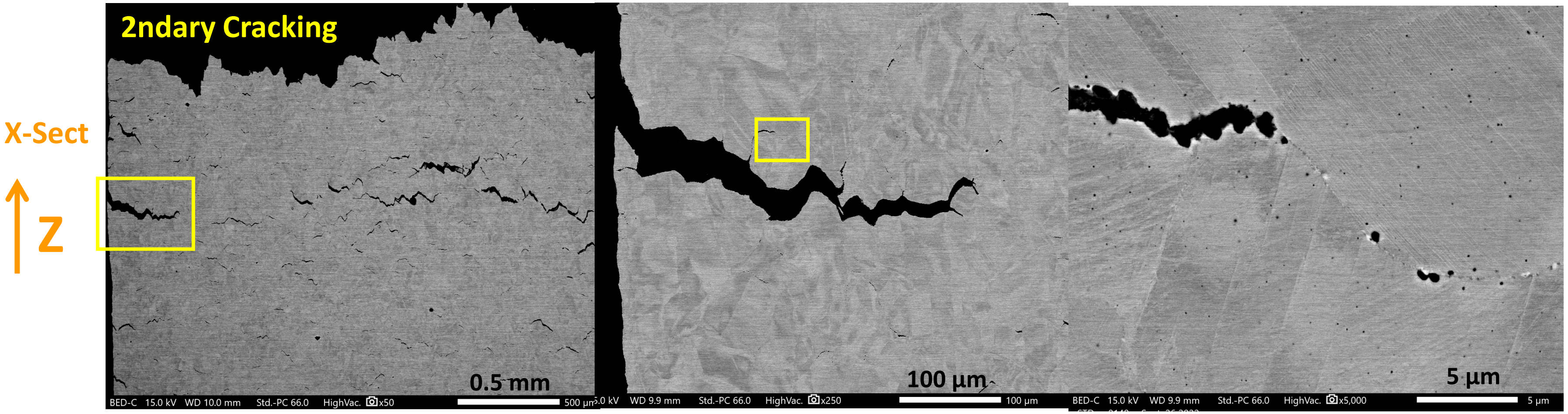
High temperature creep behavior of As-solutioned L-PBF 625

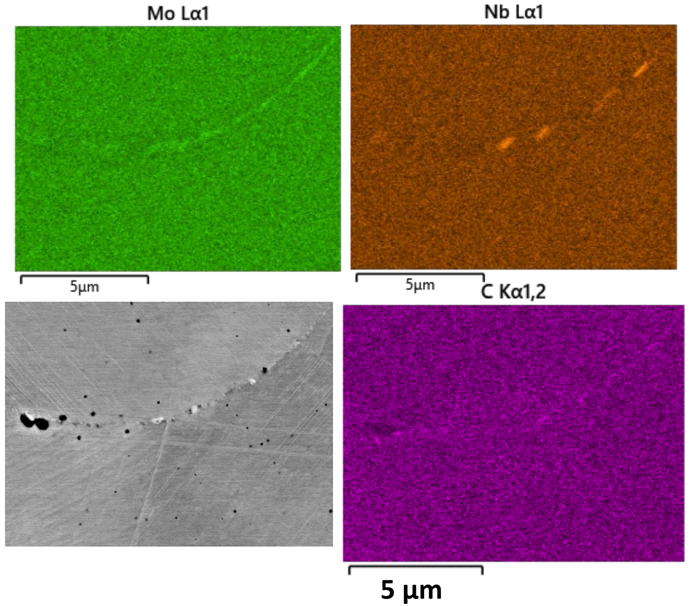
Representative Fracture - 650°C @ 400 MPa, Tf=575 h



All conditions

- Intergranular fracture
- Microvoid coalescence along GBs
- Extensive secondary cracking
- Typical dimpling from ductility
- Surface decoration of GB ppts increases with T
- Deformed grains with high dislocation density





650C Specific:

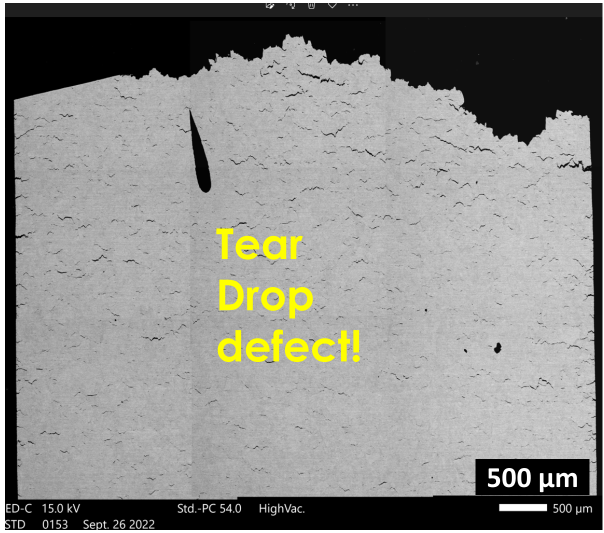
γ“-precipitates likely present at higher magnifications

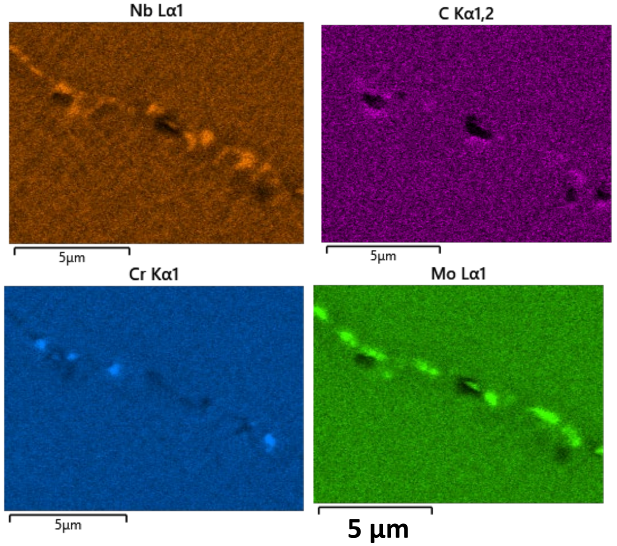
GB phases appear to be a mixture of MC and $M_{23}C_6$ carbides (or Mo segregation)

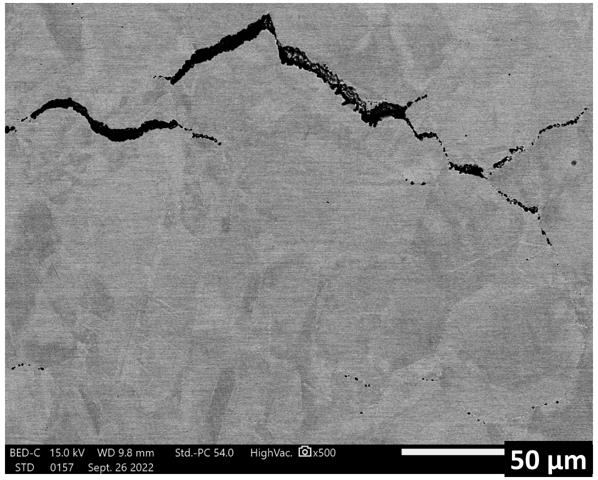
High temperature creep behavior of As-solutioned L-PBF 625

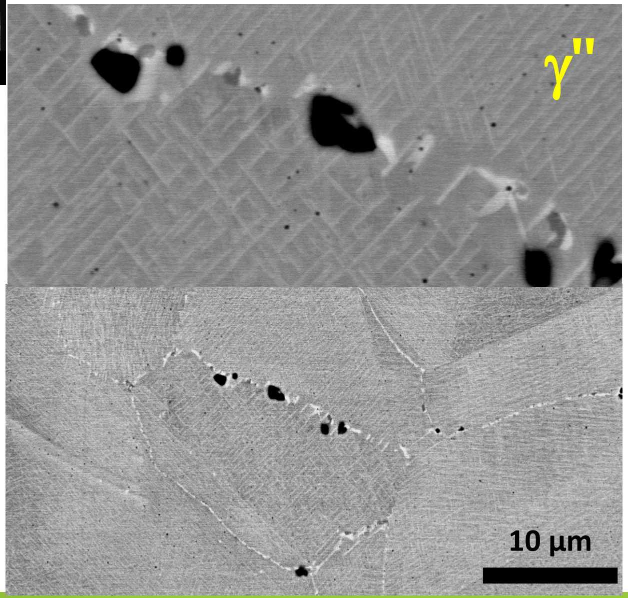
Cross-sections of failed test bars

750°C @ 200 MPa Tf= 237 h

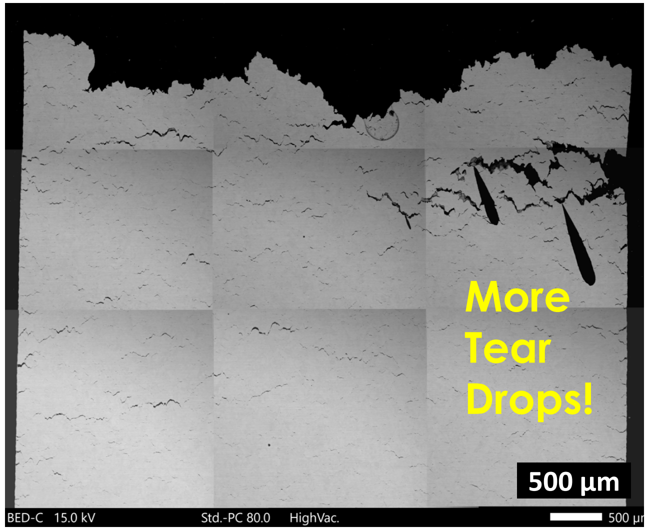


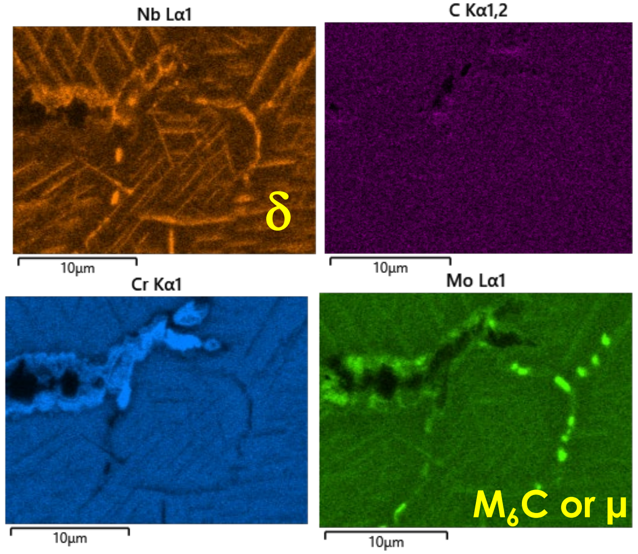


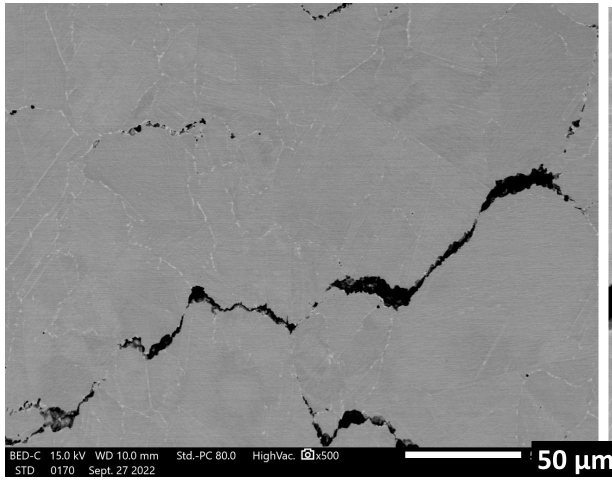


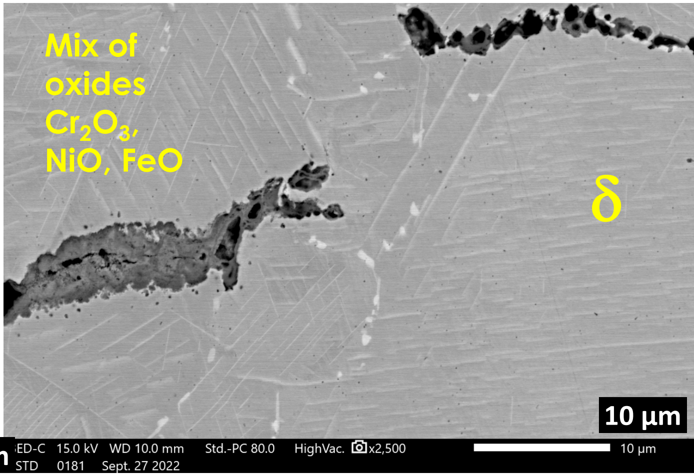


815°C @ 100 MPa Tf= 320 h









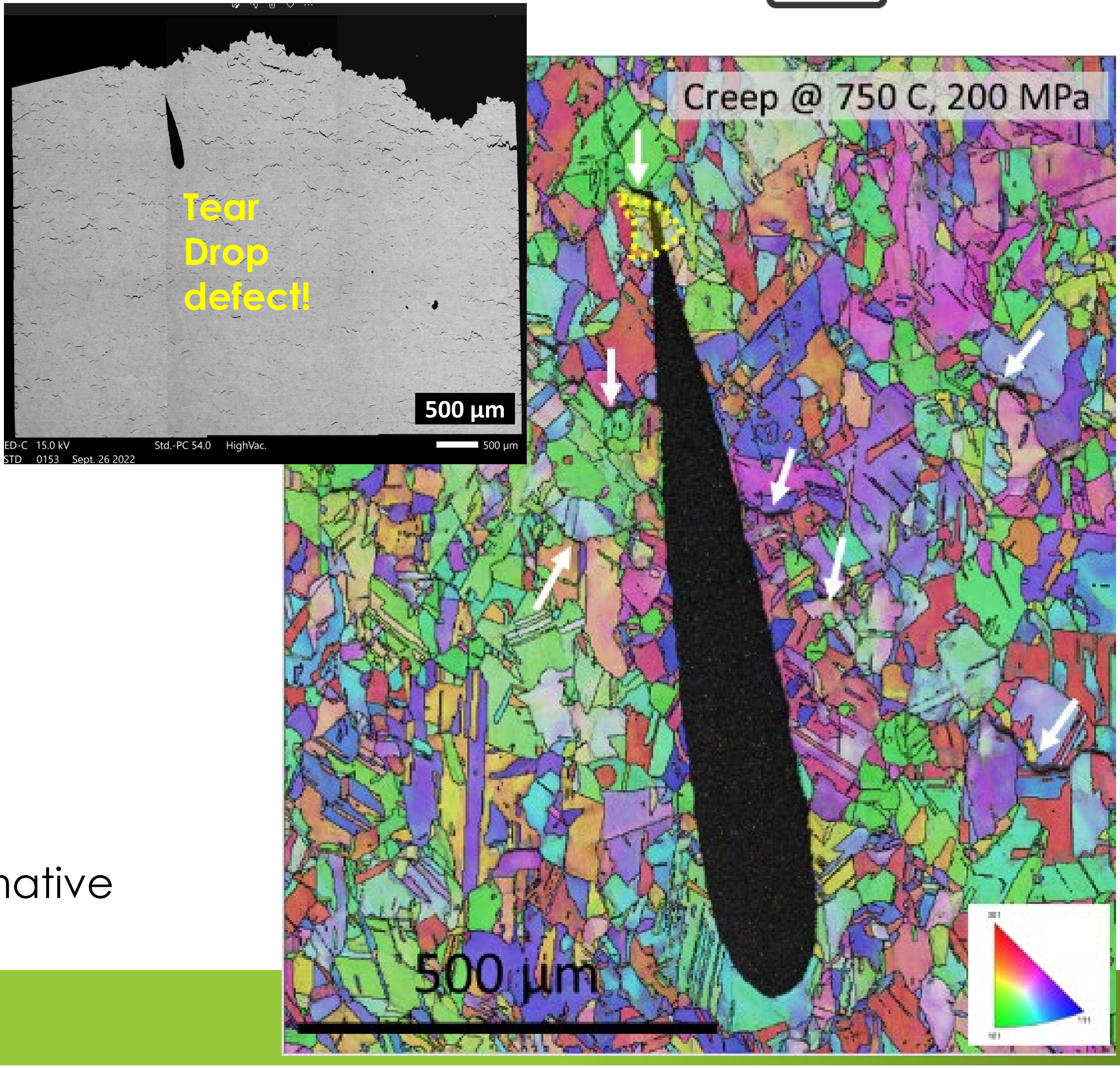
EBSD analysis confirms intragranular defect

Defect origin?

- Entrapped gas from powder production
  - **Defect too large**
- Keyhole pores tend to show irregular shapes in the as-deposited state
  - **Unlikely**
  - **Process optimized: Keyhole pores tend to be present at high energy densities**
- Any possible grain elongation due to creep deformation appears insignificant
- Smoothness suggests and that it could be still be native to the process →

Ar gas flow in EOS M290?

Test bar position on build plate would be informative



Tear drop defects in L-PBF 625 creep samples

Observed in couple crept test bars

Processing Defect → Original Shape or Crept Shape?

Why important? Such gross defects expected to impair fatigue performance

Systematically look non-destructively at two (2) samples each:

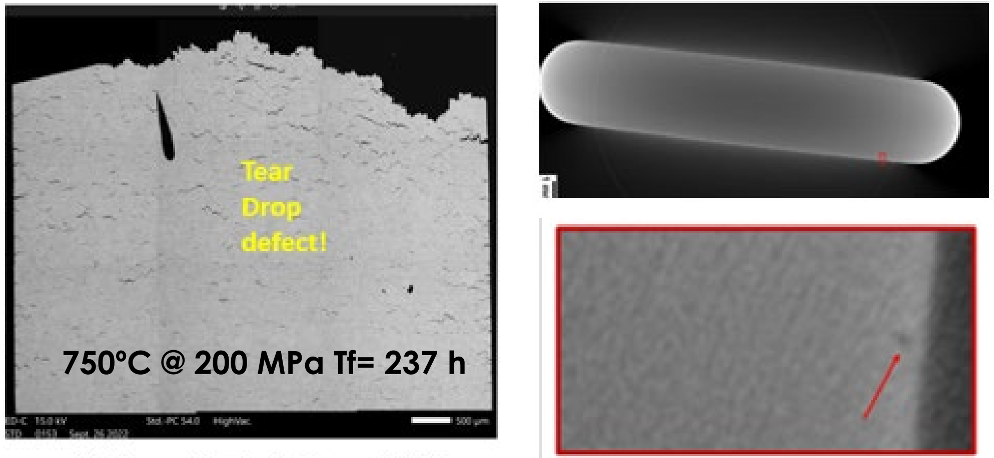
- As-printed coupon pieces (no heat treatment)
- Fully heat treated test bar blanks prior to testing (spares)
- Crept test bars after testing

CT scanner easily resolved secondary cracks internal to creep bars

Also observes edge small pores along edges associated with contour scans

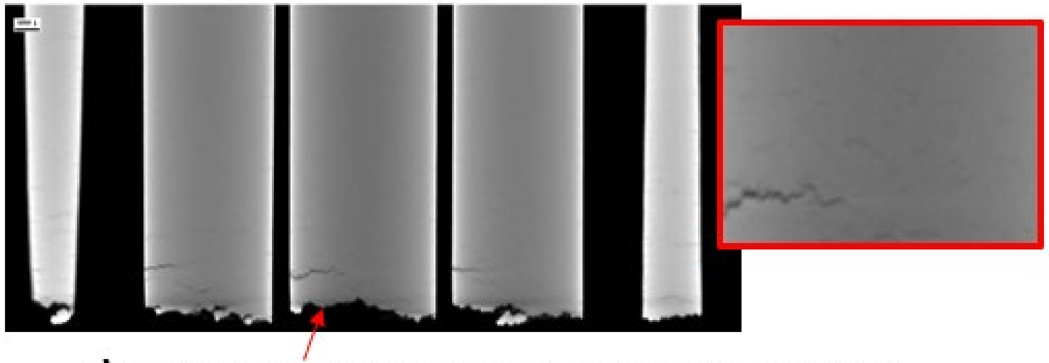
No gross defects observed! → ***Origin remain unidentified. Observations suggest a scarce defect***

CT examination at NETL MGN (POC: D Crandall)



a) Crept Test Bar TO3
(the half evaluated by SEM)

b) As printed M2-U (CT)



c) Crept Test Bar TO3 (the other half evaluated by CT)

Fully Heat treated L-PBF 625, 718, 282

Grain structure is important to performance / properties & will be used for model-based property predictions

Optimized printing parameters used

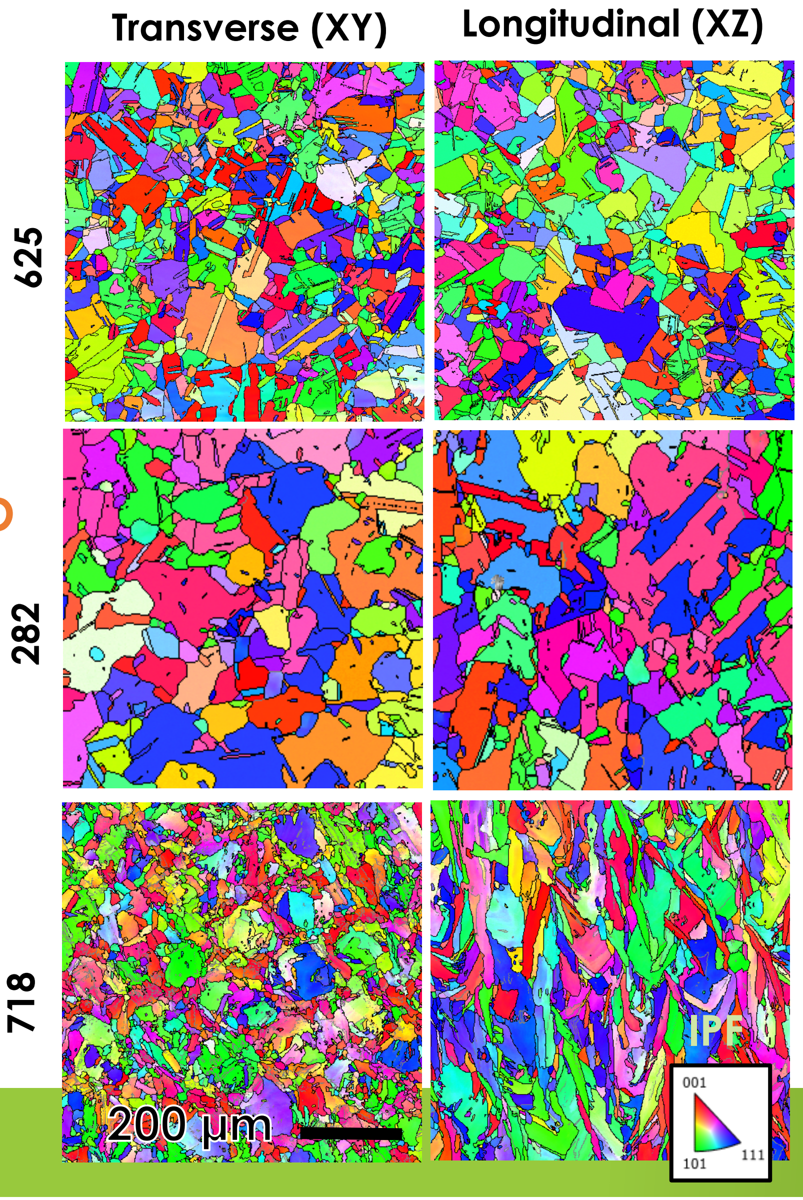
Standard commercial heat treatments

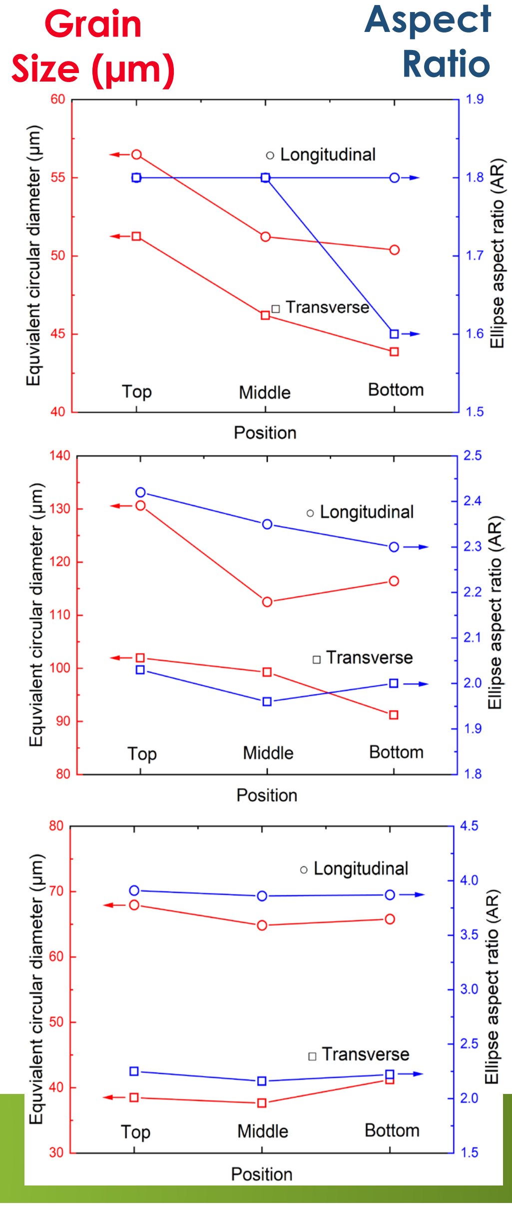
Location-specific grain structure analysis with EBSD (> 3000 grains per condition)

Recrystallization in 625 and 282 → ~ Equiaxed

Restrained grains in 718 → Aspect ratio of 4:1 in the build direction

- **Solutioned below δ-Solvus**
- **Directional performance more likely**





Environmental resistance screening at 750°C

Screen isothermal oxidation in lab air

- **750°C** ~ Injector face max operation temp.
- **Select points up to 2020 h** to ascertain growth rates
- **Machined vs. Printed → impact of surface condition:** Outer surfaces vs. internal passages

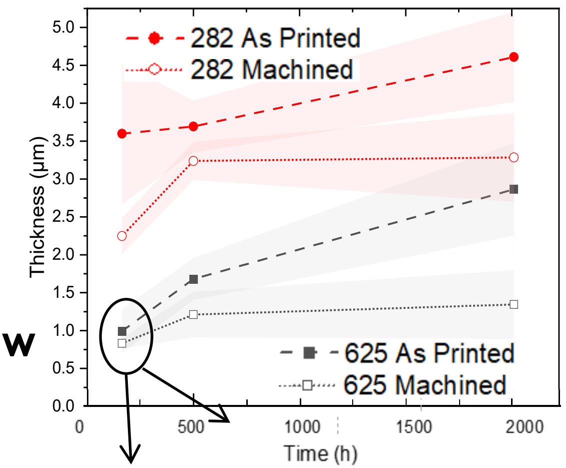
High Cr contents in 625, 718, 282 leads to slow growing, primary protective chromia scale

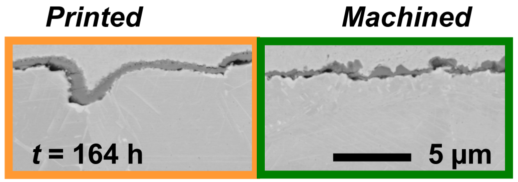
- Oxide ranged from 0.2 - 5 µm in thickness
- Oxidation rate: 282 > 625 > 718 (Not shown)

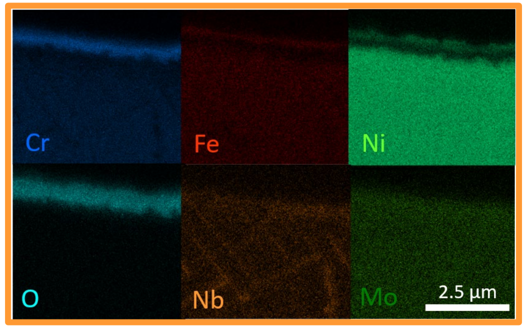
Two surface conditions show distinct differences

- **Oxide thickness in 625, 282**: Printed > Machined
- **Alloy 625**:
  - **Printed**: Uniform thickness, double layer oxide (Ni,Fe)O + Cr_2O_3
  - **Machined**: Varying thickness, Cr_2O_3 only

Oxide Thicknesses



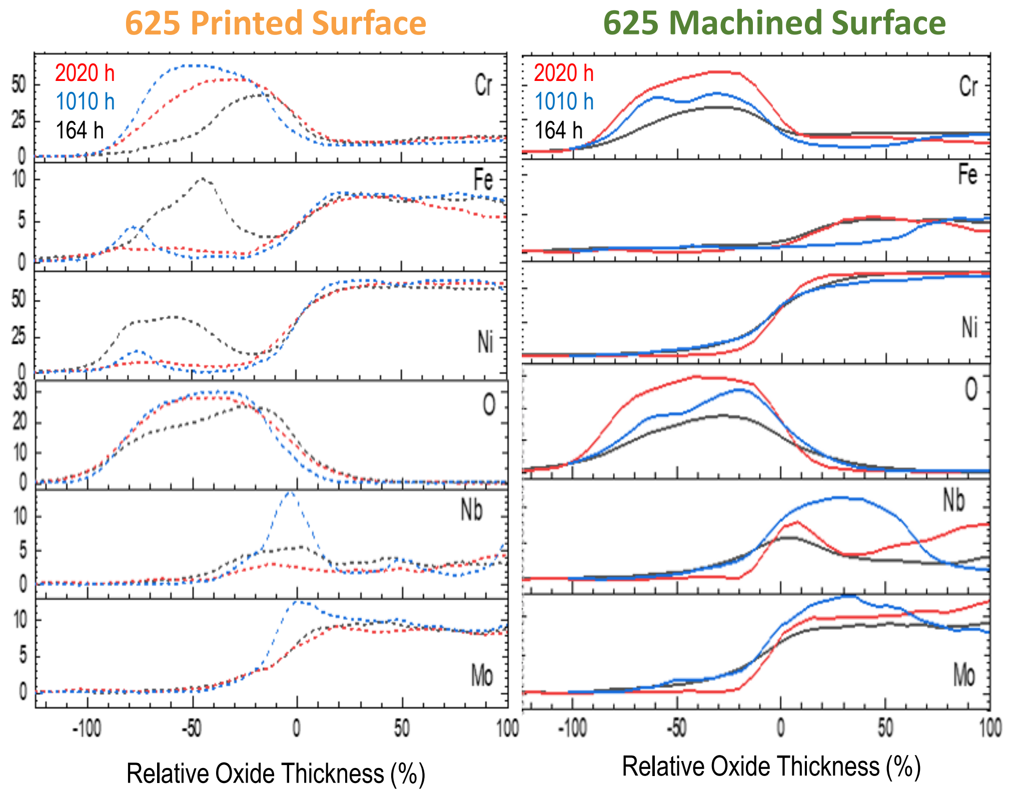




Measured Composition (XRF)

Wt.%	Ni	Cr	Mo	Nb	Fe	Ti	Al	Co	C
L-PBF 625	61.5	21.3	9.1	3.7	4.0	0.08	0.06	0.08	0.0124
L-PBF 718	52.9	18.7	3.1	5.16	18.3	0.96	0.48	0.21	0.0525
L-PBF H282	58.1	19.2	8.8	0.05	0.11	2.12	1.22	10.3	0.0459

Average line composition profiles through oxide (wt.%)

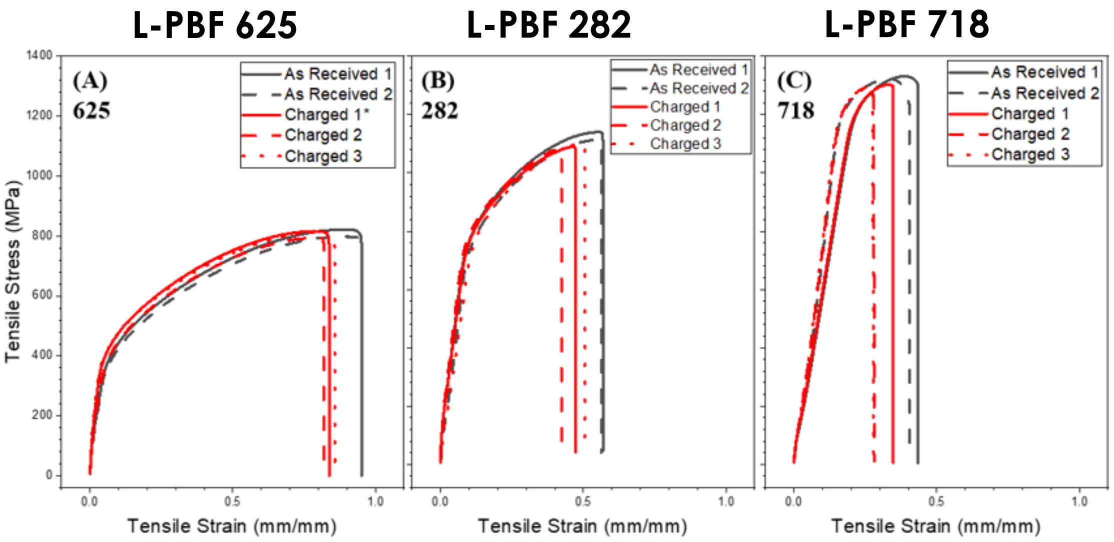


Slow strain-rate testing to screen HE

Hydrogen Embrittlement (HE)

Thickness= 1.8 mm, 20.3 mm gage length

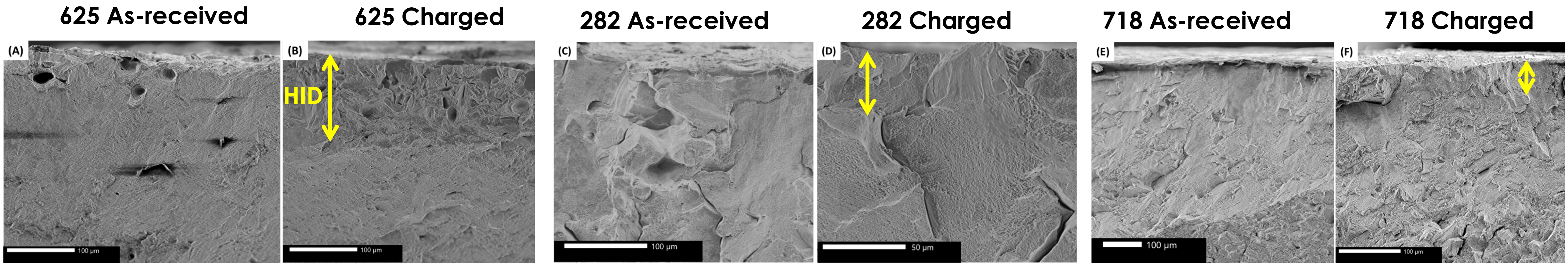
- Ex-situ electrochemical charge for 72 hours then tested 6.3 x 10-6 s^{-1}
- HE Index: L-PBF 718 > 282 > 625
- *Accepted for publication in AMPP 2023 Proceedings (Teeter et al)*
- **625 is largest H_2-Ingress Depth (HID)**



$$HE_{index} = \frac{\epsilon_{AR} - \epsilon_{HE}}{\epsilon_{AR}}$$

72-hour charge	HE Index
IN625	11.9% ± 2.0%
H282	17.7% ± 7.3%
IN718	27.3% ± 6.5%

Edge of fracture surfaces:

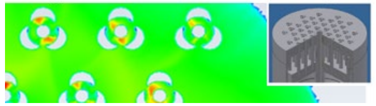

625 As-received
625 Charged
282 As-received
282 Charged
718 As-received
718 Charged

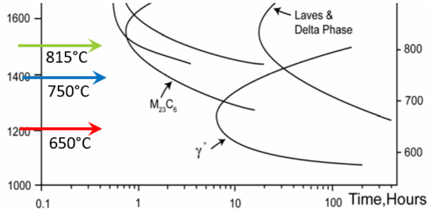
← Recrystallized grains after FHT →

← Restrained grains →

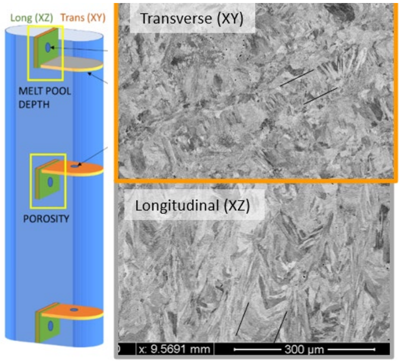
Summary

L-PBF 625 - Comparable to Wrought

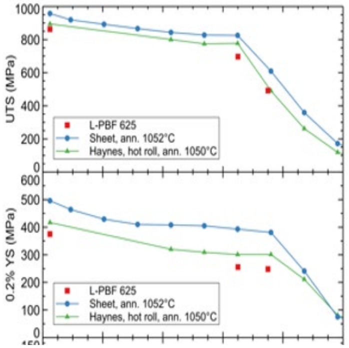




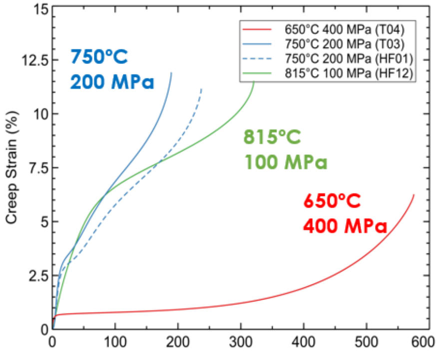
Printed Microstructure

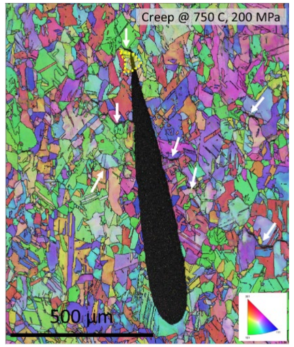


Tensile



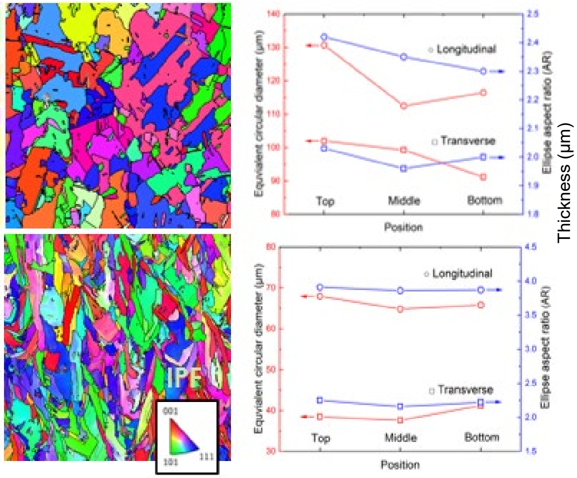
Creep



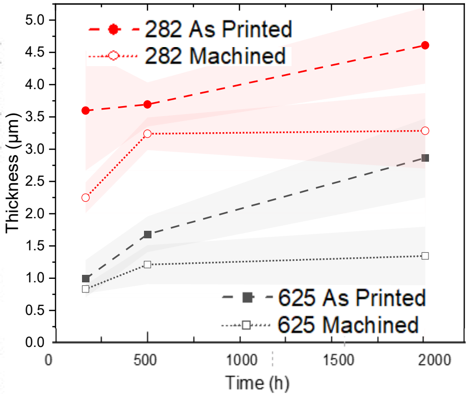


L-PBF 625, 718, 282 :

Location specific GS



750 °C Oxidation



Hydrogen Embrittlement

72-hour charge	HE Index
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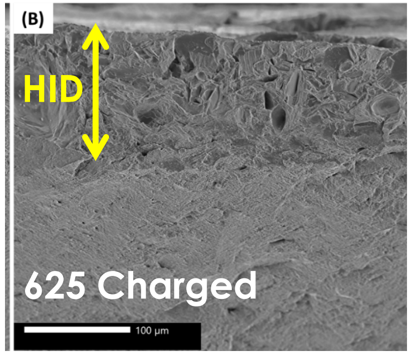

Future work:

- 718/282 Creep up to 815 °C
- 625/718/282 LCF at 650 °C
- More extensive testing in H2 → higher temp/ pressure, in-situ tensile / crack growth
- Screen materials behavior under conditions that mimic service

Thank you for your attention! Follow up questions: chantal.sudbrack@netl.doe.gov