

Technical basis for understanding the processmicrostructure-property correlation in LPBF 316 SS

Nuclear Science and Engineering Division

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ANL-AMMT-014

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September 2024

ABSTRACT

To qualify the laser powder bed fusion (LPBF) 316H stainless steel (SS) for structural use in advanced nuclear reactors, a thorough understanding of the process-microstructure-property correlation needs to be developed. This report provides an overview of ANL's research effort towards this goal in Fiscal Year (FY) 24. Specifically, the research has focused on three key areas:

- Effect of powder chemistry on the printing parameter window and on the tensile properties of printed materials: Within the multiple batches of powders procured that have chemistry variations within the specified compositional range, it was discovered that the optimum printing parameter window was not significantly impacted and the materials printed with different powders have comparable tensile behaviors from room temperature (RT) to 750°C.
- 2) Thermal aging effect on microstructure and tensile behavior: Microstructural characterization on LPBF 316H aged at 550, 650 and 750°C for 10,000 h showed that the precipitation in the LPBF material is probably 2-5 times faster than the conventional material, likely due to the presence of high densities of dislocations and boundaries. When tension tested at their corresponding aging temperatures, the 550°C aged samples show a continued drop in strength and ductility as the aging time gets longer, which can possibly be explained by the gradually weakened dynamic strain aging (DSA) due to the solutes starting to form precipitates. The 650°C and 750°C aged samples showed a plateau in strength until 2500 h of aging at 650°C and 500 h of aging at 750°C, followed by a decrease in strength for continued aging. That is possibly due to the formation of the large intermetallic phases which are embrittling the material.
- 3) Refinement of solution annealing conditions: an in-depth study has been performed to clarify the microstructural processes during solution annealing of LPBF 316H between 1100 and 1200°C for up to 4 hours. It was discovered that the material went through recovery at 1100°C and 1150°C and recrystallization at 1200°C. *In-situ* annealing experiment with high-energy synchrotron x-ray diffraction measurement revealed the kinetics of dislocation recovery at 1100°C and led to the recommendation that a recovery treatment of 1 h was sufficient as the recovery rate became diminishingly small afterward. The built-in oxide had a critical role in preventing a full recovery of dislocations. RT tension tests and creep tests at 725°C, 100 MPa showed that the recovered material had higher strength and better creep resistance (in terms of creep rate) than the recrystallized material, which was rationalized with microstructure-based deformation models. A recommendation of recovered material over recrystallized material for the ASME code case is made.

These results contribute towards establishing the technical basis for qualifying LPBF 316H SS for advanced nuclear reactor applications.

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1 Introduction

Additive manufacturing (AM) is an emerging fabrication technique to create three-dimensional (3D) components. In the nuclear industry, AM has gained attention for its capability to incorporate innovative component design, advance new materials development, embed sensors for real-time monitoring, provide onsite repairment, fabricate obsolete parts, and so on. The US Department of Energy (DOE), Office of Nuclear Energy (NE)'s Advanced Materials and Manufacturing Technologies (AMMT) program has an overarching vision of accelerating the development, qualification, demonstration and deployment of advanced materials and manufacturing technologies to enable reliable and economical nuclear energy. Based on current use and AM readiness for materials, 316H stainless steel (SS) manufactured by laser powder bed fusion (LPBF) has been chosen by the AMMT program as the first target material for design improvements, materials optimization and rapid qualification [1].

The 316H SS is a high-carbon variant of 316 SS developed for use in elevated temperature services above 500°C. Per ASTM A213/A213M Standard Specification for Seamless Ferritic and Austenitic Alloy-Steel Boiler, Superheater, and Heat-Exchanger Tubes [2], 316L should have a Carbon concentration below 0.035 wt. % while 316H should have it in between 0.04-0.10 wt.%. The higher carbon concentration in 316H promotes the formation of carbides during prolonged service at elevated temperatures and therefore, it has higher strength and better creep resistance. The conventional wrought form of 316H SS is one of the six qualified materials in the American Society of Mechanical Engineers (ASME) Boiler and Pressure Vessel Code (BPVC) Section III, Division 5, Class A construction for high-temperature reactor construction. Similarly, to utilize LPBF 316H SS for high-temperature reactor construction, it needs to be included in the code. It is expected that an optimized LPBF 316H SS will have minimized microstructure heterogeneity, be less sensitive to in-process thermal signatures and less dependent on geometrical effects, and have an improved radiation, corrosion and heat resistance [1]. In order to achieve this, research efforts are needed to develop optimized manufacturing parameters and heat treatments and to have a thorough evaluation of its performance at nuclear-relevant service conditions. In addition, research efforts are also needed to consider machine/site variability and powder batch variability which are unique to the AM processes.

This two-year research project takes the challenge to provide the technical basis for the application of LPBF 316H SS for high-temperature reactor applications through a comprehensive study conducted across Argonne National Laboratory (ANL), Oak Ridge National Laboratory (ORNL) and Los Alamos National Laboratory (LANL). We aim to examine variations in machines, sites and powder compositions on process window and microstructure. We aim to understand the effects of processing and post-processing conditions on residual stress, porosity and microstructure of LPBF 316 SS through *in-situ* monitoring and post-build characterization and identify the key parameters that have the most influence on materials performance. We plan to conduct scoping tests to understand the effects of processing conditions on materials performance in nuclear-relevant conditions. These efforts will help to understand the variability that is expected within the nuclear supply chain and help to transfer the understanding gained within the program to industrial partners.

In fiscal year (FY) 23, research at ANL has focused on three key areas: 1) Optimizing laser processing parameters on a Renishaw AM400 machine; 2) Understanding the correlation between post-build treatment and microstructure that included stress relief, solution annealing, and hot isostatic pressing; 3) Investigating the effect of thermal aging at 550°C, 650°C and 750°C up to 2500

h on microstructures and tensile behaviors. In FY 24, ANL continues the study on the thermal aging effect with samples aged to 10,000 hours becoming available. In addition, the powder chemistry effect, particularly on the optimum laser process window and the tensile properties, are evaluated. Furthermore, with supporting evidence that prefers a solution-annealed material over a stress-relieved material for the ASME code case (work in progress), a thorough investigation on the solution annealing conditions and their consequences on microstructure and mechanical performance is performed.

This report summarizes the results from FY 24 and provides recommendations. The work contributes towards establishing the technical basis for qualifying LPBF 316H SS for advanced nuclear reactor applications.

2 Materials and methods

2.1 Materials

Four batches of powders have been acquired in support of this work from Praxiar Inc. (currently Linde plc) between 2021 and 2024, labeled as Prax-AM316H-1 to Prax-AM316H-4. Their composition are within the range of UNS S31609 (316H SS) as specified in ASTM A213/A213M [2]. Table 2.1 lists the compositions of the powders provided by Praxair. For Prax-AM316H-1 batch, an independent analysis was performed by Luvak Inc.. Samples from materials printed by a Renishaw AM400 machine using those powders were also analyzed by Luvak Inc.. Those results are included in Table 2.1.

		ASTM UNS S31609	Powder	Powder	Build	Powder	Build	Powder	Build	Powder	Wrought
Designation			Prax- AM316 H-1	Prax- AM316 H-1	Prax- AM316 H-1	Prax- AM316 H-2	Prax- AM316 H-2	Prax- AM316 H-3	Prax- AM316 H-3	Prax- AM316 H-4	Heat 8092297
Order qua (kg)	ntity		50			200		500		1000	
Provided by		ASTM A213/A2 13M *	Praxair	Luvak	Luvak	Praxair	Luvak	Praxair	Luvak	Praxair	[3]
Compositi on	Fe	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.
(wt.%)	Cr	16.0- 18.0	17.6	17.00	17.04	16.8	17.33	17.0	17.42	16.7	17.25
	Ni	11.0- 14.0	12.3	12.00	12.22	12.1	11.52	12.3	12.50	11.9	13.48
	M o	2.00- 3.00	2.6	2.58	2.57	2.5	2.45	2.3	2.61	2.6	2.34
	M n	2.0*	1.03	1.11	1.09	1.13	1.01	1.05	0.88	0.02	1.86
	Si	1.00*	0.41	0.45	0.45	0.48	0.50	0.07	0.061	0.04	0.58
	С	0.04- 0.10	0.05	0.053	0.040	0.06	0.053	0.08	0.076	0.07	0.057
	0		0.05	0.051	0.046	0.03	0.017	0.03	0.014	0.02	
	N		0.01	0.014	0.015	0.01	0.013	0.01	0.015	0.01	0.030
	Р	0.045*	< 0.005	0.013	0.018	< 0.005	0.008	< 0.005	0.006	< 0.005	0.024
	S	0.030*	0.00	0.003	0.005	0.00	0.003	0.00	0.003	0.00	0.019

Table 2.1. Chemical compositions of powders and materials utilized in this study.

* Maximum, unless a range or minimum is indicated.

The numbers in Table 2.1 are visualized in Figure 2.1. Although the source of analysis is not always the same, the results consistently show that the build material has slightly less carbon and oxygen than the powder, and slightly more nitrogen.



Figure 2.1. Visualization of chemical compositions among powders and builds.

All printing jobs were done on a Renishaw AM400 laser system located in the Metal Additive Manufacturing Laboratory (MAML) in ANL. The system uses a pulsed laser source. A Renishaw-recommended printing parameter set for 316L SS was used as the reference parameters. Table 2.2 lists the key parameters in this reference and in a variation. Both parameter sets have similar volumetric energy densities around 47 kJ/m³. The 316H materials printed with those parameters have low porosities on the level of 0.05% and similar grain structures [4]. A solution-annealed wrought 316H SS reference material (heat number 8092297) with an average grain size of 266 μ m is utilized in this study. The chemical composition of the wrought material is listed in Table 2.1.

	Scan Strategy	Laser Power (W)	Point Dis- tance (µm)	Exposure Time (μs)	Hatch Spac- ing (um)	Rotation Angle (deg)	Layer Thickness (um)
Reference	Meander	195	60	80	110	67	50
Variation 1	Meander	215	50	60	110	67	50

Table 2.2. A Renishaw-recommended printing parameter set for 316L SS

Table 2.3 summarizes the LPBF 316H builds made with the powders between FY 22 and FY 24 and the work performed with those builds.

Build	Build ID 20220603 • Prax-AM316H-1 powder • 0.05% C, 0.05% O	Build ID 20230303 Prax-AM316H-2 powder 0.06% C, 0.03% O	Build ID 20230410 • Prax-AM316H-2 powder • 0.06% C, 0.03% O	Build ID 20230811 • Prax-AM316H-3 powder • 0.08% C, 0.03% O	Build ID 20231017 Prax-AM316H-3 powder 0.08% C, 0.03% O
Photo				Real Providence	
Purpose	Tensile testing and thermal aging	 Process parameter optimization ³⁰/₄ ³⁰/₄ ³⁰/₄	Comprehensive mechanical testing	 Process parameter optimization Tensile testing and thermal aging 	Comprehensive mechanical testing

Table 2.3. Information about the 316H SS builds produced in ANL using the Renishaw AM400 LPBF machine between FY 22 and FY 24.

2.2 Thermal aging and solution annealing

Two blocks of materials from Build 20220603 were machined into SS-3 type tensile specimens for thermal aging experiment (Figure 2.2 (a) and (b)). One block has the specimens extracted in the direction perpendicular to the build direction (BD) (Figure 2.2(a)), and the other has them in the direction parallel to BD (Figure 2.2(b)). The tensile specimens had nominally a gauge length of 7.62 mm, a gauge width of 1.52 mm and a gauge thickness of 0.76 mm. Individual specimens were wrapped in tantalum foils and encapsulated in quartz tubes under vacuum. The specimens were placed in box furnaces for thermal aging at 550°C, 650°C or 750°C. For each temperature, aging times varied among 5, 25, 100, 500, 2500 and 10000 hours.

Materials and samples from Build 20230410 were also encapsulated in quartz tubes under vacuum and solution annealed in a tube furnace followed by water quenching. The annealing conditions are specified in Table 2.4.



Figure 2.2. (a) A schematic showing the specimens extracted in the direction normal to BD (denoted as H orientation). (b) A schematic showing the specimens extracted in the direction parallel to BD (denoted as V orientation). (c) A photo showing the encapsulated specimens placed in a box furnace.

Table 2.4.	List	of solution	annealing	conditions.
1 4010 2.1.	LIBU	or solution	unneunng	conditions.

Temperature (°C)	110	0	1150	1200		
Time (h)	1	2	1.5	1	2	4

2.3 Microstructural characterization with microscopy

Optical microscopy was used to characterize the porosity of the materials. As-printed parts were sliced at the locations of interest, mounted into carbon mounts with a Buehler mounting press, polished with sandpapers down to 800-grit followed with suspensions down to 1 μ m, and final polished in a vibratory polisher with 0.1 μ m suspension. The optical microscopy was performed with a Keyence VHX digital microscope at 50× and 100× magnifications and the images were analyzed for porosity and characteristics of the pores.

Scanning electron microscopy (SEM) was performed with a JEOL IT800HL microscope. Electron beam voltages of 5-15 keV were used in those experiments. Both secondary electron detector (SED) imaging and backscattered electron (BSE) imaging were used to highlight different features. Electron backscatter diffraction (EBSD) and energy dispersive x-ray spectroscopy (EDS) were performed on selected specimens to provide quantitative information on grain structures and the secondary phases.

Scanning transmission electron microscopy (STEM) in high-angle annular dark field (HAADF) and bright field (BF) imaging modes was performed with a FEI Talos F200X TEM/STEM at the Center for Nanoscale Materials (CNM) in ANL to study the microstructures of selected specimens. Specimens were mechanically polished down to 100 μ m in thickness, and 3 mm TEM disks were punched out. The disks were then jet-polished until electron transparent with an electrolyte of 5% perchloric acid and 95% methanol at -30 °C with a Struers TenuPol-5 jet polisher. EDS was used to map the chemical composition of selected areas of interest. The EDS intensity maps were converted to Quantitative Hyperspectral X-ray Maps (Q-maps) for analysis.

2.4 In-situ wide-angle x-ray scattering measurements during 1100°C annealing

A piece of the as-built material from Build 20220603 was used for *in-situ* heating experiments at the beamline 1-ID of the Advanced Photon Source in Argonne National Laboratory. The sample has a surface area of 3 mm \times 3 mm and a thickness of 0.76 mm in the transverse (i.e. normal to build) direction. The x-ray energy was 76.11 keV and the beam size was 0.13 mm \times 0.13 mm. The specimen was heated to 1100°C at 200°C/min in a Linkam heater with continuous argon gas flow and held for 1.5 hours. Simultaneously, wide-angle x-ray scattering (WAXS) and small-angle x-ray scattering (SAXS) measurements were performed at a rate of 0.05Hz using the four-detector setup at the beamline 1-ID. The WAXS detectors were calibrated with a CeO₂ powder sample (NIST standard SRM 674b). For this work, the SAXS data was not used due to the low signal levels and the uncertainties in the structure of the oxide phases.

The WAXS data was analyzed using the GSAS-II software [5]. For WAXS, signals from the upper detector panel (namely the GE1 panel) were integrated into diffraction line profiles, and the peaks were fitted with the Pseudo-Voigt function. A whole profile fitting methodology was used and the lattice parameter for each time stamp (i.e., each data file collected *in situ*) was obtained. Additionally, individual peak fitting was carried out and the full width at half-maximum (FWHM) values of each peak was obtained. Those values were used to calculate the dislocation densities in each phase, using the modified Williamson-Hall method [6]. Details of the *in situ* WAXS data analysis using the modified Williamson-Hall method have been elaborated in a number of publications, such as [7,8]. In brief, the peak broadening, after subtracting the contributions from the instrument broadening, is attributed to the presence of dislocations in the lattice; accordingly, the FWHMs are fitted linearly to diffraction vectors, which are modified to account for dislocation

contrast assuming a given fraction of edge and screw dislocations. The dislocation contrast factors were obtained using the software ANIZC [9]. At each time stamp, the intercept of the linear fitting is inversely proportional to the coherent scattering domain size D, and the slope is proportional to the square root of the dislocation density ρ . In this study, the FWHM from the {200}, {220}, {311}, {222}, {400}, {331}, {420}, {422} planes of the austenite phase were used. The {111} plane was discarded because of the intensity saturations. The R-square values from the linear fittings at all time stamps were above 0.97, indicating the high reliability of this measurement and analysis.



Figure 2.3. Schematics showing the experimental setup for the *in-situ* annealing experiment at the beamline 1-ID of the Advanced Photon Source.

2.5 Tension and creep testing

Tension tests of SS-3 type specimens were performed with two Instron Model 5980 Materials Testing Systems with the Instron Bluehill 3 testing software for control and data acquisition. The testers are equipped with 3-zone furnaces for air testing up to 1100° C. To begin a test, a specimen was installed into a grip that was designed for shoulder loading. The tips of two thermal couples were placed in close vicinity to the top and bottom region of the gauge section of the specimen to reflect the actual temperature of the specimen and to serve as the input of the furnace control. The temperature was brought up to the target gradually and a soaking period of 1 hour was applied to ensure a thermal equilibrium of the loading train. All tests were conducted with a strain rate of 0.001/s until rupture. The elastic modulus of the raw data was corrected with the known values of E = 200 GPa, 155 GPa, 146 GPa, and 134 GPa for 316 SS at RT, 550, 650 and 750°C, respectively [10].

Round-type creep specimens per ASTM E8/E8M specification, with nominal gauge lengths of 31.75 mm and gauge diameters of 6.35 mm, were machined from the as-built materials and materials with different solution annealing treatment according to Table 2.4. Creep tests were performed with ATS model 2320-MM lever arm testers under 725°C, 100 MPa in air until rupture.

2.6 Thermodynamic and kinetics simulation

The thermodynamics-and-kinetics simulation was conducted based on the Equilibrium and Precipitation modules built in the Thermo-Calc software. The TCFE13 and MOBFE8 databases were adopted. The input parameters referred to the experimental conditions, including composition, temperature, and annealing time. In the calculation of coarsening kinetics, the physical properties of the MnSiO₃ Rhodonite and the MnCr₂O₄ Spinel phases, such as interfacial energy and molar volume, were supplied to Thermo-Calc software. The particles were assumed to be spherical.

3 Chemistry effect

3.1 Chemistry effect on optimum printing parameter window

Using the Renishaw-recommended printing parameter set as the reference (Table 2.2), the laser power was varied between 115 and 275 W, the point distance between 40 and 80 μ m, and the exposure time between 50 and 110 μ m for individual cubes printed in Build 20230303 and Build 20230811. The cubes were investigated with optical microscopy for internal porosity. The result for Build 20230303 has been presented in FY 23's milestone report [4] and is included here in Figure 3.1 for comparison purposes. The scanning velocity of the laser was calculated using point distance/exposure time. The color scale in Figure 3.1 indicates the porosity levels; the polygons in those two maps outline the process windows that produce materials with better than 0.1% porosity. The reference parameter set is circled out in red in those maps. As shown in Table 2.1, the major differences between the two builds are the concentrations of carbon and silicon. For Build 20230303, carbon is 0.053 wt.% and silicon is 0.50 wt.%. For Build 20230811, carbon is 0.076 wt.% and silicon is 0.061 wt.%. Nevertheless, Figure 3.1 suggests that the optimum printing parameter window is similar between the two builds and the effect from chemistry variations as noted above is not obvious.



Figure 3.1. Maps showing the parameters used in Build 20230303 and Build 20230811 with porosity as color. The optimum printing parameter windows are outlined with polygons. The Renishaw-recommended reference condition is circled out in red in each map.

3.2 Chemistry effect on tensile behavior

Materials printed with the Prax-AM316H-1, Prax-AM316H-2 and Prax-AM316H-3 powders using the reference printing parameter set were tested under uniaxial tension from room temperature (RT) to 750°C, along with samples from the wrought material. The property data is shown in Figure 3.2 for both the vertical (i.e., gauge along build direction) and the horizontal (i.e., gauge perpendicular to build direction) specimens. The grey bars are the data from the wrought material while the bars of other colors are from the LPBF materials. Though only one specimen was tested in each condition, the results indicate that there is no substantial difference in the yield strength (YS), the ultimate tensile strength (UTS) and the uniform elongation (UEL) among the different LPBF builds. The total elongation (TEL) varies to some extent among the builds, which can be better explained with specimen variation due to internal porosity or other reasons rather

than chemistry variation. Compared to the wrought material, the LPBF materials have significantly higher YS, comparable UTS, and significantly lower UEL and TEL.



Figure 3.2. (a) YS and UTS for vertical specimens of LPBF materials printed with different powders, in comparison to wrought specimens. (b) UEL and TEL for vertical specimens of LPBF materials printed with different powders, in comparison to wrought specimens. (c) YS and UTS for horizontal specimens of LPBF materials printed with different powders, in comparison to wrought specimens. (d) UEL and TEL for horizontal specimens of LPBF materials printed with different powders, in comparison to wrought specimens.

4 Thermal aging of LPBF 316H SS

4.1 Microstructural evolution

To assess the effect of prolonged thermal exposure to the microstructure and performance of LPBF 316H SS, thermal aging at 550, 650 and 750°C was conducted on SS-3 tensile specimens fabricated from block materials printed using the Prax-AM316H-1 batch of powders (build ID 20220603). In FY 23, aging up to 2500 h has been completed; samples were studied with SEM and STEM and tension tested at their corresponding aging temperatures [4]. In FY 24, specimens aged to 10,000 h have been taken out of the furnaces. Figure 4.1 shows the SEM-BSE images of the specimens aged at 550, 650 and 750°C for 500, 2500 and 10000 h. At 550°C, fine precipitates are observable on grain boundaries after 2500-h of aging (to the resolution of SEM), and on both grain boundaries and cell boundaries after 10000-h of aging. At 650°C, precipitates with bright and dark contrast are observable after 500-h of aging and become more prevalent as the aging time increases. After 10000 h, a new phase with a greyish contrast in BSE and of micrometers in size appears. At 750°C, this greyish phase is the most prominent feature at low magnifications, which grows rapidly with time. At high magnifications, additional phases with bright and dark contrasts are present; they are oxides found in the as-printed materials.



Figure 4.1. SEM-BSE images of the specimens aged at 550, 650 and 750°C for 500, 2500 and 10000 h.

EDS mapping provides information on the compositions of phases. Figure 4.2 through Figure 4.4 summarize the precipitate phases in the materials aged to 10,000 hours at 550, 650 and 750°C based on EDS mapping. Both SED and BSE images are presented. All the materials have Mn-Si-O, Cr-C-O and Mo-Si rich phases. The Mn-Si-O rich phase is known as the MnO·SiO₂ Rhodonite, which is formed during the printing process. The Cr-C-O rich phase seems to be very similar to the M₂₃C₆ phase based on X-ray diffraction and electron diffraction results (not included in this report), so it could be that some O replaces C in the structure. The Mo-Si rich phase has a composition of 44.3Fe-34.2Mo-13.9Cr-5.7Ni-1.9Si (values in wt.%), measured by STEM-EDS, and is in reasonably good agreement with the composition of the Laves phase found in aged 316 stainless steel [11]. A Mo-Cr-Mn-Si-O rich phase is seen in the 650°C- and 750°C-10,000h aged materials (note: it is not observed in 650°C-2,500h aged material [4]). Its chemical composition is around 50.8Fe-32.6Cr-9.6Mo-5.2Ni-0.86Mn-0.55Si-0.46O (values in wt.%), in reasonably good agreement with the composition of the Sigma phase found in aged 316 stainless steel [11–13] except for the incorporation of oxygen (likely as an interstitial element). While the EDS results provide information to reasonably infer the phase types, we acknowledge that electron or X-ray diffraction is needed to confirm the crystal structures.



550°C-10,000 h

Figure 4.2. Precipitate phases in the materials aged to 10,000 hours at 550°C, based on EDS measurements.



650°C-10,000 h

Figure 4.3. Precipitate phases in the materials aged to 10,000 hours at 650°C, based on EDS measurements.



Figure 4.4. Precipitate phases in the materials aged to 10,000 hours at 750°C, based on EDS measurements.

The observation of possible phases of $M_{23}C_6$, Laves (η) and sigma at long-term aging of LPBF 316H matches with literature observations of aged conventional 316H [13,14], as shown in Figure 4.5. In those literatures, $M_{23}C_6$ is the only precipitate phase after aging at 550°C for 10,000 h, while $M_{23}C_6$ and Laves (η) phases are present after aging at 650°C for 10,000 h. After aging at 750°C for 10,000 h, $M_{23}C_6$, Laves (η), sigma and possibly χ phases are present. Table 4.1 shows that more types of precipitates are observed in 550°C- and 650°C-10,000h aged LPBF materials compared to their conventional counterparts. In fact, the precipitate types in those 10,000h aged

LPBF materials matches with those in the conventional materials aged to probably 2-5 times longer. It is possible that the high density of dislocations and boundaries in LPBF material accelerate the precipitation, in a way similar to the effect of cold work on conventional materials [13].



Figure 4.5. (a) The National Institute for Materials Science (Tsukuba, Japan) time-temperature-transformation (TTT) diagram of 316H SS, taken from [14]. (b) The TTT diagram of 316H SS solution-treated at 1260°C for 1.5 h and water quenched, taken from [13]. The red circles in both figures mark the 10,000-h aging at 550, 650 and 750°C.

	Literature on conventional 316H SS	Current work on as-built LPBF 316H
	[13,14]	
Aged at 550°C for	$M_{23}C_{6}$	(Possible) $M_{23}C_6$ and Laves
10,000 h		
Aged at 650°C for	$M_{23}C_6$ and Laves	(Possible) $M_{23}C_6$, Laves and sigma
10,000 h		
Aged at 750°C for	$M_{23}C_6$, Laves and sigma, and possibly	(Possible) M ₂₃ C ₆ , Laves and sigma;
10,000 h	χ	evidence of χ yet to be seen

Table 4.1. Comparison of precipitates between conventional and LPBF 316H materials aged to 10,000 h

4.2 Tensile properties

The evolution of microstructures during thermal aging has a profound effect on the tensile properties of the material. Figure 4.6 shows the tensile curves of aged LPBF materials tested at their aging temperatures. The curves for the wrought material are also included for comparison purposes. The curves for vertical specimens are shifted along the strain axis on each graph for better visualization. The materials in general have strong dynamic strain aging (DSA) when tested at 550°C, which becomes weaker at 650°C and disappears at 750°C. At 550°C, DSA persists in material aged to 10,000 h. At 650°C, DSA is prominent in the 500-h aged material but disappears in the 2,500-h and 10,000-h aged materials.





Figure 4.6. Tensile curves of aged LPBF materials tested at their aging temperatures. (a) 550°C. (b) 650°C. (c) 750°C. The curves for the wrought material are included for comparison purposes. The curves for vertical specimens (i.e., specimens with gauge direction parallel to the build direction) are shifted along the strain axis on each graph for better visualization.

Figure 4.7 plots the values of YS, UTS, UEL and TEL of the LPBF materials as a function of aging time. Figure 4.8 plots the true strength of the materials as a function of aging time, true strength being the true stress at the UTS point and calculated as $\sigma_{TS} = \sigma_{UTS}(1 + \varepsilon_{UEL})$. Key observations are discussed below:

Aging and testing at 550°C, the material shows a slow reduction in YS and UTS and a rapid reduction in UEL and TEL past 25 h of aging. This leads to a continued reduction in true strength, as shown in Figure 4.8. This is a surprising finding considering that the aging temperature is relatively low and the microstructural evolution, as shown in Figure 4.1, is slow. It indicates that strong thermal embrittlement is happening in the LPBF 316H material at this temperature. A possible explanation is related to DSA, as manifested by the serration on the tensile curves. The mobile solutes that interact with dislocations and cause DSA, such as carbon, oxygen, silicon and chromium, are forming precipitates during aging which reduces the magnitude of DSA. However, DSA is a hardening mechanism in austenitic stainless steels because dislocations pinned by solute atoms have their cross-slip restricted and have to go with planar slip, which promotes dislocation pileups rather than mutual annihilation, which in turn raises the flow stress [15]. As DSA gets weakened with solutes forming precipitates, the gradual loss of this hardening mechanism resulted in the reduction in strength and ductility.

Aging and testing at 650°C, the material shows a slow decrease in YS and UEL and a slow increase in UTS until 2,500 h of aging. This leads to a plateau in true strength until 2,500 h of aging. At

longer aging time, the material's strength and ductility simultaneously decrease. This can be explained by the formation of possible sigma phase in the 10,000-h aged material, as shown in Figure 4.1 and Figure 4.3. The sigma phase is known to be an embrittling phase which causes loss of ductility and toughness because of its poor tolerance to strain. In addition, the large volume fraction of this phase consumed the alloying elements like Mo in the matrix, leading to a drop in strength.

Aging and testing at 750°C, the material shows a slow decrease in YS and UTS as well as a slow increase in UEL when aged up to 500 h. At longer times, the trend continues but the rate accelerates. A plateau in true strength is maintained below 500 h, after which it gradually decreases. While the possible sigma phase is readily observed in the 500-h aged sample, this time it does not directly embrittle the material; rather, the material gets significantly more ductile. A possible explanation is that this is the temperature that the static recovery of dislocations during thermal aging is prominent, leading to a significant reduction in dislocation density in the LPBF material. The precipitates initially form preferably on dislocations and boundaries, retarding the dislocation recovery process, but as the precipitates coarsen during long-term aging, the dislocation recovery process continues and the material softens while gaining back some ductility. The impact of the possible sigma phase is reflected in the accelerated decrease in strength after 500-h of aging. Similar to the 650°C-10,000h aged material, the large volume fraction of the possible sigma phase consumed the alloying elements like Mo in the matrix which resulted in a significant reduction in strength.



Figure 4.7. (a) Yield strength (YS) of the aged LPBF materials as a function of aging time. (b) Ultimate tensile strength (UTS) of the aged LPBF materials as a function of aging time. (c) Uniform elongation (UEL) of the aged LPBF materials as a function of aging time. (d) Total elongation of the aged LPBF materials as a function of aging time.



Figure 4.8. True strength of the aged LPBF materials as a function of aging time.

5 Solution annealing of LPBF 316H SS

5.1 Introduction

Solution annealing (SA) of austenitic stainless steel (SS) components is commonly performed after the forming process is done to bring carbon and other solute elements into a solid solution and to promote a single-phase microstructure. For additively manufactured (AM) austenitic SS, SA also offers a way of mitigating the microstructural inhomogeneity and property heterogeneity introduced by the rapid heating and cooling processes inherent to the laser-material interaction, aligning them more closely with those of wrought materials. This alignment could facilitate comparable and thus predictable performance, leveraging the extensive databases typically available for wrought materials which detail their mechanical properties, microstructural features, and processing parameters. Various standards have specified that the SA for the wrought form of type 316 SS shall be performed at 1020°C [16], 1040 °C [2,17–19] or 1093 °C [20] followed by water quenching or other rapid cooling methods. In contrast, there is a lack of guidance on SA practices for AM 316 SS, although a few recommendations have been made. ASTM F3184 [21] recommended that the Condition B components manufactured by powder bed fusion (PBF) shall be solution annealed in accordance with instructions for the wrought product. Some AM machine vendors provide recommendations to customers; for example, EOS GmbH has specified in their Stainless Steel 316L Material Data Sheet a holding temperature of 1150 °C for a minimum of 1.5 h when thoroughly heated, followed by water quenching [22]. These temperatures are generally higher than what are specified for wrought materials. However, the ASTM and the machine vendors have neither provided reasons behind those recommendations nor provided microstructural or mechanical information on the SA materials.

In addition to facilitating composition homogenization, performing SA treatment of AM materials serves two other functions: recovery and recrystallization. Recovery refers to the change of the deformed matrix at elevated temperatures, mainly through the reduction of dislocation density, and does not involve the long-range motion of grain boundaries. Recrystallization refers to the formation of new, strain-free crystals that gradually consume the deformed matrix. In literature, researchers have investigated annealing treatment for laser-based AM 316L SS up to 1400 °C for 1 to 4 hours [23–30]. A general observation is that the AM materials experience recovery at mid to high temperatures (600 to 1100°C range) and recrystallization at very high temperatures (1100°C and above). In contrast, for cold-worked, conventional type 316 SS, the recrystallization temperatures are generally much lower, in the 700-850°C range for cold-work levels of 30-95% [31–33]. Despite those findings, a knowledge gap exists in correlating the printed microstructure to the material's response to heat treatment and in understanding the consequence of heat treatment on mechanical performance. Additionally, in order to optimize and customize post-treatment strategies for AM materials, an understanding of the differences between the AM materials and their conventional counterparts is deemed necessary.

In this work, we present a quantitative study on the SA treatments of a laser powder bed fusion (LPBF) 316H SS in both the recovery and recrystallization regimes, detailing the microstructural evolution and unraveling the microstructure-mechanical property (tension and creep) correlation. A wrought, SA-treated counterpart is used for comparison. Analytical electron microscopy and *insitu* wide-angle and small-angle x-ray scattering (WAXS and SAXS) at a high-energy synchrotron source are utilized to provide insights into the dynamics of dislocation recovery, oxide particle evolution and recrystallization kinetics. CALPHAD-based computation is utilized to rationalize

experimental findings. The detailed characterization provides input to unveil the tension and creep mechanisms. Overall, this work clarifies key processes involved in the recovery and recrystallization regimes of an LPBF 316H SS, showcases the profound effect of microstructures on mechanical behaviors, and provides recommendations for the SA conditions of LPBF 316H SS under different considerations.

5.2 Characterization and thermodynamic simulation methods

A piece of as-built LPBF material from Build 20230410 was sectioned into small blocks and solution-annealed at 1100, 1150 and 1200°C for various durations in a tube furnace followed by water quenching. The SA conditions and the characterization methods applied are listed in Table 5.1.

Temperature (°C)	RT	1100		1150	1200		
Time (h)		1	2	1.5	1	2	4
SEM/EBSD	×	×	×	×	×	×	×
STEM/EDS	×	×			×		
In-situ WAXS		×					
Tension test at RT	×	×	×		×	×	×
Creep test at 725°C, 100 MPa	×	×					×

Table 5.1. Solution annealing conditions, characterization techniques and testing conditions utilized in this study

5.3 Solution annealing in recovery regime

Figure 5.1 shows the EBSD grain maps in Inverse Pole Figure (IPF) coloring (top row) and the Kernel Average Misorientation (KAM) maps (bottom row) of the as-built material as well as the materials solution annealed at 1100 or 1150°C for various durations. While some coarsening is observed for the small grains along the center of the melt pool paths, no substantial difference exists among the grain structures of the materials, and recrystallization does not happen.



Figure 5.1. EBSD grain maps in Inverse Pole Figure (IPF) coloring (top row) and the Kernel Average Misorientation (KAM) maps (bottom row) of the as-built material as well as the materials solution annealed at 1100 or 1150°C for various durations.

STEM bright-field images show that compared to the as-built material (Figure 5.2(a)), the 1100°C-1h and the 1150°C-1.5h SA materials (Figure 5.2(b, c)) no longer have well-defined dislocation cells in most places, but instead, they have a high density of low-angle grain boundaries (LAGBs) of polygon shapes consisting of geometrically necessary dislocations (GNDs), a recovery phenomenon known as polygonization [34]. The dislocation densities remain high within the LAGBs, having relaxed morphology and often have nano-oxides associated with them (see enlarged figures in Figure 5.2 (b, c); black arrows point to some of the oxides). Those oxides, characterized by EDS (not presented here) and confirmed by literatures [24], are MnCr₂O₄ Spinel phase, believed to be transformed during annealing from MnSiO₃ Rhodonite phase that exists on the dislocation cell walls in the as-built material (see enlarged figures in Figure 5.2 (a) ; black arrows point to some of the oxide phase that exists on the dislocation cell walls in the as-built material (see enlarged figures in Figure 5.2 (a) ; black arrows point to some of the oxide phase that exists on the dislocation cell walls in the as-built material (see enlarged figures in Figure 5.2 (a) ; black arrows point to some of the oxides). The oxides are 10-100 nm in size.



Figure 5.2. STEM bright field images showing the dislocation structures, low-angle grain boundaries (LAGBs) and oxide particles (some are pointed by black arrows in enlarged figures) in (a) the as-built material, (b) the 1100°C-1h SA material, and (c) the 1150°C-1.5h SA material.

The elemental redistribution from SA treatment is quantified by EDS line scans. Multiple line scans have been performed across cell walls, LAGBs and high-angle grain boundaries (HAGBs); Figure 5.3 shows an example of cell walls. It is seen that while the as-built material has about 1.5% Cr enrichment across the wall, the 1100°C-1h material has no enrichment. The same observation applies to the other types of boundaries, indicating that the chemistry has been homogenized.



Figure 5.3. EDS line profiles showing the concentration of Cr across dislocation cell walls in (a) the as-built material and (b) the 1100°C-1h SA material.

In-situ WAXS measurement of the 1100°C SA of an LPBF 316H sample revealed the dynamics of dislocation recovery. Figure 5.4(a) and (b) plot the evolutions of dislocation density and fraction of screw dislocation, respectively. The dislocation recovery is first observed when the temperature reaches about 800°C and it progresses rapidly; by the time the temperature reaches 1100°C (in 1.7 min), the dislocation density decreases from 4.7×10^{14} /m² to 1.7×10^{14} /m², a 64% reduction. Holding at 1100°C for 1.5 hours further reduces the number to 1.1×10^{14} /m². During the annealing process, a continued drop in the screw dislocation fraction is observed until it reaches to just a few percent. An in-depth discussion about the dislocation recovery mechanism is provided in Section 5.6.1.



Figure 5.4. The evolution of (a) dislocation density and (b) screw dislocation fraction during the heating-up and the 1100°C-holding stages measured by *in-situ* WAXS.

5.4 Solution annealing in recrystallization regime

When the temperature is increased to 1200°C, recrystallization happens. Figure 5.5(a) shows the EBSD grain maps and the KAM maps for LPBF 316H samples annealed at 1200°C for 1, 2 and 4 hours. The EBSD maps of the reference wrought material are also included, which show larger grains (266 µm on average) than the 1200°C-4h material (130 µm on average). The recrystallized grains present low KAM values which are easily identifiable in the KAM maps (deep blue regions). The recrystallized grains have equiaxed shapes and often have annealing twins. It is seen that under 1200°C for 4 hours, over 90% of the volume was recrystallized. The average grain sizes and average KAM values are plotted in Figure 5.5(b) for all the as built and SA LPBF 316H materials. It is seen that annealing at 1100-1150°C for up to 1.5 hours does not lead to appreciable changes in those two parameters. However, at 1200°C the recrystallization takes place and new grains grow rapidly, resulting in a steep reduction in KAM. The trend is the same between the building and the transverse directions. Figure 5.5(c) is an SEM-BSE image of the 1200°C-1h material, showing both the recrystallized and non-recrystallized grains (original grains). The non-recrystallized grains have large orientation variations within them and contain a large number of small oxide particles. The oxide particles present a dark contrast in the SEM-BSE image. On the other hand, the recrystallized grains have minimal internal orientation variations and have fewer but larger oxides, especially at the grain boundaries (GBs). The effect of the oxides on grain recovery and recrystallization will be elaborated in Section 5.6.2.



Figure 5.5. (a) EBSD grain maps in IPF coloring and the KAM maps for LPBF 316H samples annealed at 1200°C for 1, 2 and 4 hours, as well those for the wrought material. (b) The average grain size and the average KAM values for the as-built and the SA materials involved in this study. (c) An SEM-BSE image of the 1200°C-1h material, showing both the recrystallized and non-recrystallized grains (original grains). The oxide particles have a dark contrast.

STEM images of the recrystallized and un-recrystallized grains in the 1200°C-1h material are shown in Figure 5.6(a) and (b), respectively. The recrystallized grains have very low densities of dislocations and oxide particles. Large oxide particles of a few hundred nm in size are observed to be on or near GBs and twin boundaries (TBs). In contrast, the un-recrystallized grains have a high density of polygon-shaped LAGBs and line dislocations. Reminiscences of the dislocation cell structure can still be observed, although the "cell walls" are as thin as a few dislocation lines, as seen in Figure 5.6(b) insert. Small oxide particles of 10-100 nm are often associated with those dislocation lines and LAGBs, similar to the observations in the 1100 and 1150°C SA materials as shown in Figure 5.2 (b, c).



Figure 5.6. STEM images revealing the microstructures of (a) a recrystallized grain and (b) some unrecrystallized grains in the 1200°C-1h material.

5.5 Tension and creep behavior of solution annealed samples

The engineering stress-strain (s-s) curves from the room-temperature uniaxial tension tests on the wrought, LPBF as-built and LPBF SA samples are shown in Figure 5.7(a). The yield strength (σ_{YS}), ultimate tensile stress (σ_{UTS}), uniform elongation (ε_{UEL}) and total elongation (ε_{TEL}) values are listed in Table 5.2. SA treatment lowers σ_{YS} of LPBF 316H samples; the more aggressive the treatment, the softer the material. After 2 or 4 hours at 1200°C, σ_{YS} is very close to that of the wrought material. The SA materials have high strain-hardening capacities with values between 0.74 and 1.26 as calculated by ($\sigma_{UTS} - \sigma_{YS}$)/ σ_{YS} . In contrast, the strain-hardening capability of the as-built material is only 0.28 due to its inherent high dislocation density.



Figure 5.7. (a) The engineering stress-strain curves of the wrought, the as-built LPBF, and the different SA LPBF 316H materials tension tested at room temperature. (b) The creep curves of the the wrought, the as-built LPBF, and the different SA LPBF 316H materials tested at 725°C under 100 MPa.

	$\sigma_{\rm YS}$ (MPa)	$\sigma_{\rm UTS}$ (MPa)	$\sigma_{\rm PIS}$ (MPa)	$\varepsilon_{\mathrm{UEL}}$ (%)	ε_{TEL} (%)
Wrought	250	568	967	70.2	78.9
As-built	489	628	970	54.5	66.9
1100°C-1h	335	583	1020	74.9	85.4
1100°C-2h	314	566	997	76.1	88.9
1200°C-1h	274	538	959	78.2	91.0
1200°C-2h	257	540	964	78.6	91.4
1200°C-4h	243	589	1050	78.4	93.5

Table 5.2. Room-temperature tensile parameters of the wrought, the as-built LPBF, and the different SA LPBF 316H materials.

On the other hand, the time-dependent property, particularly the creep property, is more complicated. Figure 5.7(b) shows the creep-rupture curves of the wrought, the as-built, the 1100°C-1h and the 1200°C-4h LPBF materials at 725°C, 100 MPa. 100 MPa is below the 0.2%-offset yield point for all materials at 725°C. The rupture time, rupture strain, minimum creep rate, time to 1% strain and time to onset of tertiary creep (determined by a line with a 0.2%-strain-offset from the tangential line to the minimum creep point) values are listed in Table 5.3. The LPBF materials have low rupture strains compared to the wrought material; aggressive solution annealing is helping with the issue at the expense of a faster creep rate. The as-built LPBF material has one order of magnitude lower minimum creep rate than the wrought material, but with recrystallization during 1200°C-4h SA, it is nearly the same as the wrought. The as-built and the 1100°C-1h SA materials have prolonged secondary creep stages, as indicated by their long time to tertiary creep compared to the other two materials. This suggests that the microstructural features unique to the LPBF process, including the high densities of dislocations, boundaries and oxide particles, play key roles in providing high creep damage resistance. Detailed discussions on the tension and creep behaviors are provided in Sections 5.6.3 and 5.6.4, respectively.

	Rupture time	Rupture	Minimum	Time to 1%	Time to onset
	(h)	strain (%)	creep rate	strain (h)	of tertiary
			(%/h)		creep (h)
Wrought	490	46.3	0.019	45	77
As-built	419	3.6	0.0018	280	325
1100°C-1h	538	11.8	0.0077	51	330
1200°C-4h	377	18.6	0.019	42	91

Table 5.3. Creep parameters of the wrought, the as-built LPBF, and the different SA LPBF 316H materials tested at 725°C under 100 MPa

5.6 Discussion

5.6.1 Static dislocation recovery during SA of LPBF material

Figure 5.4(a) revealed a key finding in the SA treatment with *in-situ* WAXS: the initial dislocation recovery is a rapid process which starts during the heating-up period when the temperature reaches

800°C, and by the time the temperature reaches the target of 1100° C, about 64% of recovery is achieved. Continued annealing at 1100°C for 1.5 hours only futher reduced the density by ~ 12%. Similar rapid kinetics has been reported by Jandaghi *et al.* [35]; they heated LPBF 316L SS to 1300°C and, with ex-situ XRD, observed that the majority of the dislocation recovery was found in the sample annealed for just 10 seconds. Dislocation recovery is driven by the stored energy. Accorduing to a model proposed by Kuhlmann [36] and Borelius et al. [37]the kinetics of recovery can be described as

$$\frac{\mathrm{d}P}{\mathrm{d}t} = -K_0 P \exp\left(-\frac{Q_0 - \beta P}{RT}\right)$$

where dP/dt refers to the decrease of stored energy per unit volume, P, with annealing time t, Q_0 is the activation energy of recovery, R is the universal gas constant, and K_0 and β are two materials constants independent to the temperature T. Assuming that the strain energy induced by dislocations is the main contributor of the stored energy, P can be calculated as P = $\frac{Gb^2}{2}\rho\left[f_s + \frac{1-f_s}{1-v}\right]$ [38], where G, b, ρ , f_s , v refer to the shear modulus (a function of temperature according to [39]), the Burgers vector value (0.255 nm), dislocation density, fraction of screw dislocation, and Poison's ratio (0.27), respectively. The in-situ WAXS analysis provides the evolution of ρ and f_s during the entire annealing process (Figure 5.4 (a, b)). The evolution of P with annealing time is plotted in Figure 5.8. Note that the initial ~ 6 min corresponds to the heating process, but the data presented starts from ~ 4 min when the temperature reaches 800°C and a drop in dislocation density is first observed. The recovery during the heating and the 1100°C-holding stages are considered seperately as the dislocation structure evolves (Figure 5.2 (a, b)). By applying the recovery kinetics model, the activation energies Q_0 for these two stages are fitted to 166.5 kJ/mol and 234.8 kJ/mol, as shown in Figure 5.8. The lower Q_0 in the heating-up stage indicates lower energy barrier. Fan et al. [40] studied the recovery kinetics of an LPBF 316L SS and a 10% cold-rolled conventional 316L SS by applying the same recovery model but using ex-situ hardness measurements at 750, 800 and 900°C. Unlike our in-situ anealing experiment, the ex-situ technique was not able to probe the hardness change during the heating stage of an experiment. They reported the activation energies is 213.9 and 151.4 kJ/mol, respectively, for the LPBF material and the coldrolled material. The results in the present work yield similar activation energies between the LPBF 316H SS in the 1100°C-holding stage and the LPBF 316L SS in Fan et al.'s work, and similar activation energies between the LPBF 316H SS in the heating stage and the cold-rolled conventional 316L SS in Fan et al.'s work. Such findings are discussed from microstructure and chemistry perspectives as below.

The large difference in Q_0 (166.5 vs. 234.8 kJ/mol) between the heating stage and the 1100°Cholding stages in the LPBF 316H SS can be understood by considering the dislocation structure and the oxide particles. In the heating-up stage, the annihilation of dislocation dipoles via thermally-activated climb is the dominant recovery mechanism [41,42]. The dislocation dipoles are concentrated in the cell walls [27]. Such a microstructure is similar to that of the 10% coldworked 316 SS, which also has the dislocation tangles and possible cells [43,44]. Indeed, Q_0 from the heating stage in the LPBF 316H material (166.5 kJ/mol) is similar to that of the 10% coldrolled conventional 316 SS (151.4 kJ/mol [40]). In fact, those Q_0 values are close to the activation energy for boundary diffusion in 316 SS ($Q_b = 167$ kJ/mol [45]), indicating that the dislocation cell walls and LAGBs are rapid diffusion paths that facilitates the dislocation recovery. Following the rapid anihlation of close-spaced dislocation dipoles which happens in the heating stage, in the 1100°C-holding stage, the remaining dislocations in the LPBF material are either the GNDs on the LAGBs or the line dislocations within the subgrains pinned by oxide particles (Figure 5.2(b)). It is known that the GNDs have significantly slower recovery than the other networks because they cannot simply annihilate each other [42]. For the dislocations pinned by oxide particles, additional energy is needed for the dislocations to proceed with annihilation. Both mechanisms raise Q_0 . The Q_0 of 234.8 kJ/mol in this stage is much higher than the activation energy of boundary diffusion and is close to the activation energy of lattice diffusion in 316 SS ($Q_v = 280$ kJ/mol [45]), indicating that bulk diffusion will be required to proceed further with the dislocation recovery.



Figure 5.8. The evolution of the stored energy of dislocations as a function of time during the *in-situ* annealing experiment. The fitted lines using different activation energies for the heating-up stage and the 1100°C-holding stage are also shown.

5.6.2 Recrystallization kinetics

Our work showed that for an LPBF 316H SS, 1200°C is required to facilitate recrystallization in hours. In literatures, for LPBF 316L SS, 1100°C or higher are the reported recrystallization temperatures [29]. The significantly higher recrystallization temperatures in LPBF SS compared to cold-worked conventional SS can be understood by considering the effect of dislocation and other deformation features on the nucleation regime of recrystallization. Although the dislocation density in a as-built LPBF material is similar to a 5-20% cold-worked material in the mid- 10^{14} /m² range [46,47]; other features are not quite the same. In the as-built LPBF 316 SS, as we discussed in Section 4.2, the dislocations are mainly the statistically stored dislocations concentrated in cell walls (Figure 5.2), which are readily to be recovered by thermally-activated climb when heated above 800°C (Figure 5.4). Those dislocations do not contribute to misorientations and thus do not promote the nucleation of new grains. On the other hand, in the cold-worked conventional 316 SS, besides dislocations, prominent features also include stacking faults, nano twins, shear bands, or even nano grains [43,44]. All these features are preferred nucleation sites of new grains [30,34,43]. as they have high stored energy and represent local orientation gradients necessary for nucleation. Therefore, the energy barrier to recrystallization in those cold-worked conventional materials is much lower compared to the as-built LPBF materials, leading to the lower recrystallization temperatures.

In the growth regime, the recrystallization kinetics depends on the driving pressure $P = P_D$ – $P_{\rm ZS} = 0.5\rho G b^2 - \frac{3f\gamma_{\rm GB}}{2r}$. The parameter $P_{\rm D}$ is the driving pressure for static recrystallization computed by the dislocation density (ρ), shear modulus (G = 36.4 GPa at 1200° C) and the burgers vector (b = 0.254 nm). The component P_{75} refers to drag force applied by the randomly distribued oxides, a.k.a the Zener-Smith pining, which is a function of the particle volume fraction (f), particle radius (r), and grain boundary energy. According to a previous research [48], the γ_{GB} of 316 SS is 930 mJ/m² at 1200°C. If we assume a dislocation density and oxide particle population similar to the as-built material ($\rho = 4.7 \times 10^{14} \text{ m}^{-2}$, f = 0.000331, r = 14.8 nm), P_D and P_{ZS} are calculated to be 0.55 MPa and 0.032 MPa, respectively. However, we know that there is a rapid recovery of dislocation during the heating period of annealing (see Figure 5.4(a) and Section 4.2). The dramatic decrease of dislocation density lowers the driving pressure to less than 0.17 MPa when achieving a temperature higher than 1100°C. In parallel, the oxide volume fraction reduces by about 1/3 while the size does not change much when the temperature gets to around 1100°C (Error! **Reference source not found.**), so P_{ZS} shall be less than 0.021 MPa when the temperature gets to 1200°C, and continues to drop as the oxide particles coarsen at such a high temperature which is accelerated by the moving of new grain boundaries that facilitates pipe diffusion throughout the volume [29]. Nevertheless, the presence of oxide particles likely reduces the driving pressure by about 10%, and thus has a mild role in retarding the growth of new grains.



Figure 5.9. EBSD maps for (a) 1200°C-1h, (b) 1200°C-2h and (c) 1200°C-4h SA materials with the colored areas corresponding to the recrystallized regions and the dark areas corresponding to the unrecrystallized regions. (d) The evolution of recrystallization fraction *Xv* as a function of annealing time. A fitting using the JMAK model is also shown.

The grain orientation spread (GOS) maps, reflecting the orientation variations within individual grains, are shown in Figure 5.9 (a-c) for the three EBSD maps on the LPBF materials annealed at 1200°C for different times. The colored and dark areas corresponds to the recrystallized and unrecrystallized regions, respectively, using a maximum orientation spread value of 2° as the threashold for determining a recrystallized grain. The recrystallization fraction can thus be measured. The kinetcis of recrystallization is evaluated using the Johnson-Mehl-Avrami-Kolmogorov (JMAK) model, $X_v = 1 - e^{-Bt^n}$, where X_v is the recrystallization fraction, t is the annealing time, and B and n are two constants that can be fitted via a linear regression of ln ln $[1/(1-X_v)]$ vs. ln(t), as shown in Figure 5.9(d). A fitting yields n=2.03. This value was reported to be 2.2 for LPBF 316L annealed at 1100°C [49], 0.44-1.16 at 1150°C [28,29], and 0.44 at 1200°C [49]. The variations among the *n* values for LBPF materials, and the fact that they all deviate from the ideal conditions of $n \sim 4$ assumed by the classical JMAK model, *i.e.*, random distribution of nucleation sites and stored energy [34], are likely related to the unique and varying microstructures relevant to the printing conditions. Tuning the printing conditions has been demonstrated to be an effective way to control the recrystallization kinetics and thus control the materials microstructure. For example, Gao et al. [50] developed a method to program the microstructure and properties of the AM samples based on the local control of recrystallization kinetics, in which the hatching spacing was intentionally varied within a build to modify the GND density and element segregation at the local regions of the builds. Future work is needed to develop a comprehensive model in correlating the recrystallization kinetics with the printing parameters for LPBF 316H SS.

5.6.3 Effect of microstructure on tensile strength

Figure 5.7(a) and Table 5.2 show that the as-built, the 1100°C-1h and the 1100°C-2h LPBF materials have the room-temperature σ_{YS} of 489, 335 and 314 MPa, respectively. The dislocations and the oxide particles are considered as the major contributors to the high strength in those materials. Quantitatively, $\Delta \sigma_d = M \alpha G b \rho^{0.5} (d \text{ for dislocation; work hardening})$ and $\Delta \sigma_p =$ $\frac{0.4MGb}{\pi\sqrt{1-v}}\frac{\ln\frac{r\pi}{2b}}{L_P}$ (p for particle; Orowan looping) [51–53]. In these equations, M, G, v, and b represent the Taylor factor (3.06 for FCC material), shear modulus (77 GPa at room temperature [46]), Poisson's ratio (0.27), and Burgers vector value (0.255 nm), respectively. The parameter α corresponds to the barrier strength of dislocations which is typically around 0.2 for 316 SS. The dislocation density ρ is obtained from the *in-situ* WAXS measurement (see Section 3.1; 1100°C-1.5h data is used for the 1100°C-2h sample). The mean particle radius r is obtained by measuring multiple STEM images, and the mean particle spacing L_P is calculated using $L_p = r \times [(2\pi/3f)^{0.5} 0.5\pi$] assuming the particles are randomly distributed spheres with f being the measured particle volume fraction. $\Delta \sigma_d$ and $\Delta \sigma_p$ are calculated and the results are shown in Table 5.4. $\Delta \sigma_{p+d}$ is the summation of $\Delta \sigma_d$ and $\Delta \sigma_p$. Accordingly, $\sigma_{YS} - \Delta \sigma_{p+d}$ should reflect the material's intrinsic strength plus the contribution from solute strengthening. A good agreement in $\sigma_{YS} - \Delta \sigma_{p+d}$ is observed among the as-built and the 1100°C SA materials. For the 1200°C SA materials, Figure 5.7(a) shows that their σ_{YS} are approaching that of the wrought, indicating that the soft, recrystallized regions in those materials yield first during deformation, resulted in σ_{YS} close to the wrought. In the subsequent deformation, since the unrecrystalied regions has low strain-hardening capability, the overall strain-hardening is low for the 1200°C-1h and 1200°C-2h materials, resulted in their s-s curves below that of the wrought. As the recrystallization is nearly complete in the 1200°C-4h material, its s-s curve closely follows that of the wrought.

	ρ (/m²)	r (nm)	f	<i>L_p</i> (μm)	$\Delta \sigma_p$ (MPa)	$\Delta \sigma_d$ (MPa)	$\begin{array}{c} \Delta \sigma_{p+d} \\ (\text{MPa}) \end{array}$	σ _{YS} (MPa)	$\sigma_{YS} - \Delta \sigma_{p+d}$ (MPa)
As-built	4.7×10 ¹⁴	11.1	2.1×10 ⁻ 3	0.33	114	261	375	489	114
1100°C- 1h	1.2×10 ¹⁴	14.5	2.0×10 ⁻ 3	0.45	90	132	222	335	113
1100°C- 2h	1.1×10 ¹⁴	19.5	2.0×10 ⁻ 3	0.60	71	126	197	314	117

Table 5.4. The quantification of microstructural features (dislocations and oxide particles) and their contributions to the yield strength of LPBF materials.



Figure 5.10. The true stress-strain curves of the wrought, the as-built LPBF, and the different SA LPBF 316H materials tension tested at room temperature.

Despite the differences in $\sigma_{\rm YS}$ and $\sigma_{\rm UTS}$ among all materials, the plastic instability stress $S_{\rm PIS}$, defined as the true stress at the maximum load, $S_{\rm PIS} = \sigma_{\rm UTS}(1 + \varepsilon_{\rm UEL})$, are within 1000±50 MPa for all materials, as seen in Figure 5.10. In fact, by shifting the true s-s curves of the as-built, the 1100°C-1h and the 1100°C-2h samples by 13%, 3% and 2% strain, respectively, the true s-s curves from all materials fall on top of each other. A similar exercise has been carried out by Byun *et al.* in studying the tensile behavior of irradiated steels [54]. Both Byun's work and ours imply that while the dislocation and defect structures differ, they are equivalent to some level of cold work in the work-hardening and only the applied true stress matters.

5.6.4 Effect of oxide particles and subgrain structures on minimum creep rate

The creep data presented in Figure 11 and Table 5 show that the effect of microstructure on the creep behavior of a material is profound. According to the Ashby map of type 316 SS [55,56], creep testing at 725°C and 100 MPa is within the power-law creep regime dominated by dislocation glide/climb. The effect of secondary phase particles (oxides and the precpitates formed during creep) on the creep behavior of the material can be rationalized in the form of a threshold stress, $\sigma_{\rm th}$, due to the attractive interaction between lattice dislocations and those particles. Note that only intragranular particles are accounted for rather than those on the grain boundaries. Literature reports that $\sigma_{\rm th}$ is proportional to the Orowan stress $\Delta \sigma_{\rm p}$ (p for particle) for the dispersion strengthened steels, $\sigma_{\rm th} = C * \Delta \sigma_{\rm p}$, with *C* in the range of 0.4-0.7 and decreasing with increasing temperatures as the dislocations can more easily climb over the particles or detach from them [57,58]. As noted in Section 5.6.4, $\Delta \sigma_{\rm p}$ is expressed as $\Delta \sigma_{\rm p} = \frac{0.4MGb}{\pi\sqrt{1-v}} \frac{\ln \frac{\pi \pi}{2b}}{L_{\rm p}}$, where G = 55 GPa being the shear modulus of 316 SS at 725°C. The contribution to $\Delta \sigma_{\rm p}$ from the oxides, $\Delta \sigma_{\rm oxide}$, are

listed in Table 5.5. The contribution to $\Delta \sigma_{\rm p}$ from the precipitates formed during the creep test, such as carbides and Laves phase, $\Delta \sigma_{\rm prec}$, have not yet been experimentally determined, but it's unlikely that they will be larger than $\Delta \sigma_{\rm oxide}$ because those precipitates tend to coarsen quickly at 725°C. Table 5.5 lists the assumed values of $\Delta \sigma_{\rm prec}$ for each material. For the wrought and the 1200°C-4h materials, $\Delta \sigma_{\rm prec}$ is assumed to be zero because their minimum creep rates are found at the beginning of the tests. The much higher $\Delta \sigma_{\rm prec}$ for the as-built LPBF material compared to the other materials is attributed to the dislocation cell structure and the elemental segregation on the boundaries in this material that facilitate a heavier precipitation. The corresponding $\sigma_{\rm th}$ values are calculated using a *C* value of 0.4 and are listed in Table 5.5.

Consequently, the effective stress, σ_{eff} , applied to the material during the creep test can be expressed as:

$$\sigma_{\rm eff} = \sigma_{\rm appl} - \sigma_{\rm th},$$

where σ_{appl} is the applied stress of 100 MPa. The values of σ_{eff} are listed in Table 5.5

The minimum creep rate can generally be described by the following equation [53]:

$$\dot{\varepsilon}_{\rm m} = A \frac{DGb}{kT} \left(\frac{\sigma_{\rm eff}}{G}\right)^n,$$

where A is a constant, D is the diffusion coefficient, k is the Boltzmann constant, T is the absolute temperature, and n is the stress exponent. $\dot{\varepsilon}_{\rm m}$ has been plotted against $\sigma_{\rm eff}$ in Figure 5.13; a stress exponent n=3.3 has been determined. Although this calculation has a large uncertainty, mainly due to the inaccurate values of C and $\Delta \sigma_{\rm prec}$, an exponent of 3.5 falls into the range of literature reported values of 3 to 5 on dispersion-free alloys [57], suggesting that by considering a threshold stress from the microstructural features like secondary phase particles, the effective stress is a viable explanation to the creep performance of LPBF 316H materials with different heat treatments.

	r _{oxide} (nm)	$f_{ m oxide}$	$L_{\rm oxide}(\mu m)$	$\Delta \sigma_{\text{oxide}}$ (MPa)	$\Delta \sigma_{\rm prec}$, assumed value (MPa)	$\sigma_{\rm eff}$ (MPa)
Wrought				0	0	100
As-built	11.1	2.1×10 ⁻³	0.33	81	50	47.6
1100°C-1h	14.5	2.0×10-3	0.45	65	5	72.4
1200°C-4h	55	0.4×10-4	12.5	3	0	98.8

Table 5.5. The quantification of microstructural features (grains, dislocation cells, oxide particles) and related





5.7 Recommendations on solution annealing of LPBF 316H

The results and discussions show that the SA treatment on LPBF 316H SS involves complicated micro processes besides the chemistry homogenization. The end product falls in two categories: recovered or recrystallized. The recovered material still has footprints of the manufacturing process with dense dislocations, small oxide particles and LAGBs. The recrystallized material, on the other hand, is essentially a reformed material approaching the wrought material in microstructure and behavior.

From this study on the process-microstructure-property correlation in solution-annealed LPBF 316H SS, the following recommendations are made particularly for structural applications of this material in advanced nuclear reactors:

1) Recovered materials are recommended over recrystallized materials mainly for four reasons. First, if not treated properly, partial recrystallization leaves the material with a bimodal grain size distribution that may results in anisotropic mechanical performance. Second, the coarse oxide particles in recrystallized materials may negatively impact ductility and fatigue strength, similar to what happened to the PM-HIP 316H SS [59]. Third, recovered materials have higher yield strengths and better creep resistance in terms of low creep rates compared to the recrystallized materials, potentially opening up the design window. Last, recovered materials largely maintain the as-built grain structures, and thus have the freedom to be "tuned" via changing manufacturing parameters from a materials engineering point of view for optimized performance in specific applications, a major advantage of AM.

2) An SA temperature range of 1100-1150°C and a holding time of 1 h is recommended to obtain a recovered LPBF 316H material. Holding at the recovery temperature for longer than 1 h is not necessary since the recovery rate becomes negligibly small.

3) The inclusion of oxygen in LPBF materials is almost unavoidable considering the powder production, transportation and storage costs. This study shows that the presence of oxygen in the material, in the form of nano oxide particles, is one of the key factors in slowing down the dislocation recovery during SA. The oxide particles also contribute to about 30-40% of the increased yield strength in LPBF materials (the other major contributor is dislocation) and play a vital role in providing the better creep resistance. It is yet to see if the nano oxides have any adverse effects on the materials performance, which has been observed in some PM-HIP 316H SS with coarser oxides [59]. A comprehensive study is recommended to provide a compositional range of oxygen in qualifying LPBF 316H SS.

6 Conclusion and outlook

The LPBF 316H SS possesses unique microstructures and mechanical properties compared to the conventional form of the material. To be used in nuclear reactors, the powder chemistry effect, the laser printing parameters, the microstructural stability and the performance in reactor-relevant environments need to be thoroughly studied. This study aims to provide a technical basis for qualifying LPBF 316H SS for reactor applications. Specifically, three conclusions can be drawn from the research effort in FY 24:

- The effect of powder chemistry on the printing parameter window and on the tensile properties (RT to 750°C) of printed materials was not obvious with the multiple batches of 316H powders procured that have chemistry variations within the specified compositional range.
- 2) Thermal aging had a significant effect on microstructure and tensile behavior. Microstructural characterization on LPBF 316H aged at 550, 650 and 750°C for 10,000 h showed that the precipitation in the LPBF material is probably 2-5 times faster than the conventional material, likely due to the presence of high densities of dislocations and boundaries. When tension tested at their corresponding aging temperatures, the 550°C aged samples show a continued drop in strength and ductility as the aging time gets longer, which can possibly be explained by the gradually weakened dynamic strain aging (DSA) due to the solutes starting to form precipitates. The 650°C and 750°C aged samples showed a plateau in strength until 2500 h of aging at 650°C and 500 h of aging at 750°C, followed by a decrease in strength for continued aging. That is possibly due to the formation of the large intermetallic phases which are embrittling the material.
- 3) An SA temperature range of 1100-1150°C and a holding time of 1 h is recommended to obtain a recovered LPBF 316H material for the ASME code case. When annealing the LPBF 316H at 1100 to 1200°C for up to 4 hours, it was discovered that the material went through recovery at 1100 and 1150°C and recrystallization at 1200°C. The built-in oxide had a critical role in preventing a full recovery of dislocations in the recovery regime. RT tension tests and creep tests at 725°C, 100 MPa showed that the recovered material had higher strength and better creep resistance (in terms of creep rate) than the recrystallized material, which was rationalized with microstructure-based deformation models.

In outlook, research on thermal aging of solution annealed (recovered) material and on the specification of the compositional range of oxygen is recommended. A thorough investigation on the mechanical performance of recovered materials in reactor-relevant conditions shall be carried out in preparation for the ASME code case and in developing an accelerated qualification pathway for materials manufactured with advanced technologies.

Acknowledgments

This work was supported by the U.S. Department of Energy, Office of Nuclear Energy, Advanced Materials and Manufacturing Technologies (AMMT) program, under Contract No. DE-AC02-06CH11357 with Argonne National Laboratory, managed and operated by UChicago Argonne LLC. Work performed at the Center for Nanoscale Materials and Advanced Photon Source, both U.S. Department of Energy Office of Science User Facilities, was supported by the U.S. DOE, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. The authors acknowledge support from the AMMT program with programmatic guidance provided by Meimei Li at Argonne National Laboratory, Ryan Dehoff at Oak Ridge National Laboratory and Dirk Cairns-Gallimore at the Department of Energy. Helpful discussions with Yiren Chen, Wei-Ying Chen and Mark Messner at Argonne National Laboratory, Caleb Massey and Peeyush Nandwana at Oak Ridge National Laboratory, and Robin Montoya at Los Alamos National Laboratory are gratefully acknowledged.

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