

Nitrogen Effects in Additively Manufactured Martensitic Stainless Steels: Conventional Thermal Processing and Comparison with Wrought



ERIC A. LASS, FAN ZHANG, and CARELYN E. CAMPBELL

The microstructures of additively manufactured (AM) precipitation-hardenable stainless steels 17-4 and 15-5 were investigated and compared to those of conventionally produced materials. The residual N found in N₂-atomized 17-4 powder feedstock is inherited by the additively produced material, and has dramatic effects on phase stability, microstructure, and microstructural evolution. Nitrogen is a known austenite stabilizing element, and the as-built microstructure of AM 17-4 can contain up to 90 pct or more retained austenite, compared to the nearly 100 pct martensite structure of wrought 17-4. Even after homogenization and solutionization heat treatments, AM 17-4 contains 5 to 20 pct retained austenite. In contrast, AM 15-5 and Ar-atomized AM 17-4 contain < 5 pct retained austenite in the as-built condition, and this level is further decreased following post-build thermal processing. Computational thermodynamics-based calculations qualitatively describe the observed depression in the martensite start temperature and martensite stability as a function of N-content, but require further refinements to become quantitative. A significant increase in the volume fraction of fine-scale carbide precipitates attributed to the high N-content of AM 17-4 is also hypothesized to give rise to additional activation barriers for the dislocation motion required for martensite nucleation and subsequent growth. An increase in the volume fraction of carbide/nitride precipitates is observed in AM 15-5, although they do not inhibit martensite formation to the extent observed in AM 17-4.

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I. INTRODUCTION

MARTENSITIC precipitation-hardenable (PH) stainless steels are the most popular class of PH stainless steels, providing an excellent combination of high strength and good corrosion resistance in a wide variety of environments. This class of alloys is widely used in aerospace, marine, chemical, and other industries. Of the available alloys, 17-4 is the most common, providing high strength and mechanical properties that can be tuned to meet the needs of specific applications by using various aging heat treatments.^[1,2] A variation of the 17-4 alloy, 15-5, was originally designed to provide

improved fracture toughness compared to 17-4 by using cleaner melt processing techniques and by eliminating the presence of δ -ferrite in the microstructure.^[3,4] The 15-5 alloy is also widely employed; however, the higher manufacturing costs have prevented it from completely replacing 17-4. The composition specifications for 17-4 and 15-5 are given in Table I, along with those for the cast alloy analog of 17-4 (17-4-C), described in detail in Aerospace Material Specification 5355 (AMS-5355).^[5]

Both 17-4 and 15-5 are fully BCC (body-centered cubic)/martensitic wrought alloys, with 17-4 typically containing a small amount of δ -ferrite, a consequence of its higher Cr-content. Precipitation strengthening is achieved through the precipitation of nanometer-scale Cu-rich precipitates during aging at temperatures between 753 K and 893 K (480 °C and 620 °C). Both alloys have similar materials properties, with 15-5 typically having higher yield strength and fracture toughness and 17-4 exhibiting better corrosion behavior for some heat treatment conditions. Both alloys are also considered weldable, making them a popular choice for application in additive manufacturing processes.^[1-4]

Additive manufacturing (AM) has received significant attention as a direct component fabrication technique in recent years due to its potential to produce one-off parts and parts on demand without expensive machinery, to

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Table I. Composition Specifications for 15-5 PH, 17-4 PH, and Modified CB-7Cu-1 (Cast 17-4 PH Analog, Described in Detail in AMS-5355^[5])

Element	17-4 PH ^a	15-5 PH ^a	17-4-C ^b
Fe	bal.	bal.	bal.
Cr	15.0–17.5	14.0–15.5	15.5–16.7
Ni	3.0–5.0	3.5–5.5	3.6–4.6
Cu	3.0–5.0	2.5–4.5	2.8–3.5
Mn	< 1.0	< 1.0	< 0.7
Si	< 1.0	< 1.0	< 1.0
Nb	0.15–0.45	0.15–0.45	0.15–0.40
C	< 0.07	< 0.07	< 0.06
N	N/S	N/S	< 0.05
P	< 0.040	< 0.040	< 0.025
S	< 0.030	< 0.030	< 0.025

All compositions are given in mass fraction times 100. “N/S” indicates a composition limit is not specified.

^aSpecifications for 15-5 PH and 17-4 PH include Ta in the Nb composition (*i.e.*, Nb + Ta), and sometimes include a specification for Mo (< 0.5 pct).

^bAMS-5355 also includes specifications for Ta (< 0.05 pct), Al (< 0.05 pct), and Sn (< 0.02 pct).

generate less scrap material, and to potentially lower costs. AM offers the potential to produce the complex, high value, low volume parts required for many aerospace and military applications with fewer subcomponents, less assembly time, or possibly with new, more efficient design geometries impossible to produce *via* traditional processing routes. As a result, AM of martensitic PH stainless steels is of great interest for aerospace and military applications. However, 15-5 and 17-4 were originally designed as wrought alloys, while AM processing conditions are considerably different. Although conventional welding is similar to AM processing, building an entire structure *via* welding results in a dramatically different thermomechanical history than simply joining two parts together, and consequently the AM microstructures and properties are quite different compared to welded material.

Not only are the AM processing conditions vastly different than conventional forming methods, but the processing history of the gas-atomized powder feedstock used in most AM processes can produce a material that is chemically different than conventional materials.^[6–8] Nitrogen gas is often used in the gas-atomization of stainless steel powders. However, N is not inert in steels, and behaves similar to C, substituting for C in various carbide phases, and promoting the formation of other carbide/nitride phases. Nitrogen also acts to stabilize the FCC (face-centered cubic)-austenite phase, similar to C. 17-4 powder produced by N₂ gas-atomization can contain as much as 0.15 pct N*^[6,9,11], while N₂

*All compositions are given in mass fraction times one hundred unless otherwise stated. For example, an alloy with a N-content of 0.15 pct, contains a mass fraction of N of 0.0015.

gas-atomized 15-5 powder contains less, typically ≤ 0.07 pct N in the AM-fabricated components,^[8,15]

although it has been reported to be as high as 0.11 pct in the as-received powder.^[16,17]

This residual N, along with the AM processing conditions, produce microstructures and properties of AM martensitic PH stainless steels that are significantly different than their wrought counterparts.^[6–14,18–21] Specifically, the volume fraction (*v_f*, simply referred to as “fraction”) of retained austenite (RA) present in as-built AM 17-4 can be as high as 90 pct. The lower N-content present in AM 15-5 results in a much lower RA fraction in the as-built microstructure, typically < 5 pct.^[15,16] In AM 17-4, the RA fraction can be reduced *via* post-build thermal processing, *i.e.*, homogenization and solutionization, but a significant fraction remains even after post-build thermal processing, between 5 and 20 pct.^[8,9] The RA fraction in post-processed AM 15-5 is near zero, similar to wrought material.

The as-built N₂ gas-atomized AM 17-4 also exhibits a yield-point phenomenon, arising due to segregation of C (and N) to dislocations.^[22] The upper yield stress observed in AM 17-4 is between 500 and 600 MPa, or approximately equal to the yield strength of an austenitic stainless steel, such as 304 or 316, suggesting the yield-point phenomenon is a result of the RA present in AM 17-4.^[6,18–21] Indeed, post-build thermal processing significantly reduces the observed yield-point phenomenon, though it typically cannot be eliminated.^[19,20] Further, as-built Ar- and water-atomized AM 17-4 exhibit a less pronounced (or no) yield-point phenomenon compared to N₂-atomized material.^[23,24] The RA in AM 17-4 has also been shown to be unstable with respect to applied stress/strain, leading to a strain-induced martensitic transformation upon deformation.^[6,18,20] The AM 17-4 material exhibits a transformation-induced plasticity (TRIP) effect during tensile (and compression) testing experiments. Reducing the RA fraction *via* post-build thermal processing can decrease the observed TRIP effect but does not eliminate it.^[6,18–21] As a result, the mechanical properties of AM 17-4 are very different than those expected for wrought 17-4, making direct substitution of the AM alloy for the wrought alloy impossible in critical, load-bearing applications.

The obvious solution to avoid the negative effects of N in AM 17-4 is to replace it with 15-5, which has similar mechanical properties to 17-4 in the wrought form and is less susceptible to RA formation during AM processing.^[1–4,25–27] The increased cost aside, recently AM 15-5 has demonstrated potential issues when produced using AM methods, including cracking of the AM-fabricated component during post-build thermal processing, as well as unusual precipitation hardening behavior.^[13,14] Therefore, direct substitution of AM 17-4 with AM 15-5 is not necessarily straightforward.

Water-atomized 17-4 powder is one potential alternative to N₂-atomized material but has received little attention as a potential feedstock for AM processes.^[28] This is most likely because the powder characteristics of water-atomized powder are not well-suited for the needs of AM. Water-atomized powder tends to be less

spherical and has poor flowability characteristics compared to gas-atomized powder.^[29]

Ar gas-atomization is another alternative to eliminating the issue of residual N in AM 17-4 powder.^[6–8,23,24] However, Ar is considerably more expensive than N₂. Ar-atomized powder can cost up to ten times more than N₂-atomized powder. Additionally, Ar is truly inert in most alloys, including Fe and steel, and the solubility of Ar in Fe is virtually zero. As a result, Ar can be trapped in gas pores in the feedstock powder.^[30] The rapid heating and cooling during the AM process results in the Ar gas porosity being inherited by the as-built AM material. Hot isostatic pressing (HIP) can eliminate many of these spherical pores. However, because the solubility and diffusivity of Ar are nearly zero, the Ar remains trapped as a compressed gas after the pores are closed and the pores can re-open during post-HIP annealing or while in service.^[31] Further, there has been recent evidence that the residual N in AM 17-4 may have a positive effect on corrosion resistance.^[11] It is therefore worthwhile to examine the effects of N in AM 17-4 (and AM 15-5) to understand its role in austenite stabilization and to possibly eliminate or mitigate the resulting RA and other potential microstructural and property issues.

In the present work, a combined computational thermodynamics and experimental investigation approach is taken to understand the behavior of N in AM martensitic PH stainless steels produced using laser powder-bed fusion (L-PBF). The as-built, homogenized, and solutionized microstructures of AM 17-4 and 15-5 are compared and contrasted to their wrought counterparts, with specific attention paid to the influence of residual N on the martensite transformation and resulting microstructure.

II. MATERIALS AND METHODS

A. Experimental Procedures

1. Materials processing

The N₂-atomized AM 17-4 samples were built using (Electro-Optical Systems) EOS** StainlessSteel GP1

**Mention of commercial products does not imply endorsement by NIST, nor does it imply that such products or services are necessarily the best available for the purpose.

grade powder (17-4 chemistry) on an EOS M270 laser powder-bed fusion (L-PBF) system with a standard GP1 parameter set. The AM 15-5 samples were provided by Naval Air Systems Command (NAVAIR) and were built using EOS StainlessSteel PH1 (AM 15-5) powder on an EOS M290 system and a standard EOS PH1 parameter set. The Ar AM 17-4 (EOS StainlessSteel 17-4PH) samples were built at the Applied Research Laboratory at Pennsylvania State University using an EOS M280 and a standard 17-4PH parameter set. All materials were built under a N₂ atmosphere. Wrought 17-4 bar stock (2.5 cm by 5 cm) was used to compare

with the AM-produced materials. Table II shows the compositions for all three powders and the wrought 17-4 (W-17-4). Note the suffix “-E” is used to distinguish the experimentally investigated alloy from the alloy in general. For example, AM 17-4-E identifies the specific composition of the AM 17-4 alloy used in the present experiments, while AM 17-4 refers to AM 17-4 stainless steel in general.

Heat treatments of the AM materials were performed in a laboratory scale tube furnace. Homogenization treatments were performed at 1423 K (1150 °C) for 1 hour, while solutionization treatments were performed at 1323 K (1050 °C) for 30 minutes (essentially wrought Condition A: $\approx$ 1313 K (1040 °C) for $\geq$ 30 minutes, followed by air cooling). The wrought 17-4 material was also solutionized at 1323 K (1050 °C) for 30 minutes. The samples were first sealed in vacuum-evacuated and Ar-backfilled quartz ampules to prevent oxidation. The quartz ampules were placed in the tube furnace already heated to the target temperature, and the heat treatment time was started when the furnace temperature returned to the target temperature, < 5 minutes. The encapsulated samples were removed from the furnace after the specified time and immediately quenched into a bath of room temperature water, without breaking the ampule, resulting in the sample being cooled to room temperature in a matter of tens of seconds to a few minutes, similar to an air-cooling process. This process is referred to as a no-break quench (NBQ).

2. Characterization

X-ray diffraction (XRD), optical microscopy (OM), and scanning electron microscopy (SEM) were used to characterize the microstructure of the as-built and heat-treated samples. Samples for all three characterization techniques were prepared by first cutting a piece from the sample to obtain a fresh surface (*i.e.*, unaffected by any heat treatment) using a low-speed saw to minimize the deformation imparted on the material during cutting. A fresh surface was then prepared using standard metallographic preparation techniques by grinding with SiC paper, starting with a grit-size of 240 and finishing with 1200 grit. The samples were then polished to a 1 μ m finish with diamond polishing solution. XRD analysis was performed on the polished specimens using Cu K α radiation using a scan range of 40 to 50 deg 2 θ to focus on the relative intensities of FCC (111) and BCC (110) reflections. The volume fractions of austenite and BCC/martensite[†] were esti-

[†]The tetragonality (*i.e.*, c/a lattice parameter ratio) of the martensite was found to be very close to one, making the distinction between BCT-martensite and BCC- δ -ferrite impossible using X-ray techniques. Because of this BCC/martensite is used when discussing XRD results.

mated from the measured relative intensities of these two peaks, using the direct comparison method given in Reference 32, the same method used by Meredith *et al.*^[8] Cu K α radiation is strongly absorbed by Fe, and diffraction information is limited to the first 3 to 5 μ m of a sample's surface in the 2 θ -range of interest. Because

Table II. Compositions of the Experimentally Investigated AM PH Stainless Steel Powders Used in the Present Study

Element	W-17-4-E	AM 17-4-E	AM 15-5-E	Ar AM 17-4-E
Fe	bal.	bal.	bal.	bal.
Cr	15.87	15.73	14.39	16.36
Ni	4.24	4.57	4.06	4.15
Cu	3.87	4.01	3.76	4.16
Mn	0.55	0.64	0.053	0.20
Si	0.45	0.76	0.5	0.27
Nb	0.26	0.27	0.33	0.33
C	0.02	0.04	0.01	0.02
N	N/A	0.12	0.051	0.01
P	0.026	0.007	0.014	0.014
S	0.009	0.001	0.004	< 0.001

All compositions are given in mass fraction times 100. No uncertainty was provided for the measurements.

the RA in AM 17-4 is known to be unstable with respect to deformation, great care was taken to minimize the deformation layer on the surface of the prepared sample. To minimize any possible variation in depth of the deformation layer (and possibly transformed martensite layer), samples that were to be compared directly to one another were prepared simultaneously. The damage layer was estimated to be $\leq 1 \mu\text{m}$ from an increase in the amount of RA detected using electron backscatter diffraction when the SEM accelerating voltage was increased from 5 to 20 kV. The effects of sample surface preparation were also investigated by characterizing the XRD-measured RA fraction as a function of the grit-size of the grinding paper used to prepare the surface. No appreciable difference was found in any of the samples, from the coarsest paper used, 240 grit, down to $1 \mu\text{m}$. Despite the careful sample preparation, it is possible that the damage layer thickness varied from sample to sample, causing some variation in measured RA fraction of nominally identical samples. The maximum difference in XRD-observed RA fraction in identically processed samples was about 5 pct.

To further validate the results of the RA fraction calculated using laboratory XRD measurements, synchrotron-based powder XRD experiments were performed on identically processed samples using the high-resolution XRD instrument at 11-BM-B of the Advanced Photon Source (APS), Argonne National Laboratory.^[33] The monochromatic X-ray energy was 30 keV (wavelength, $\lambda = 0.414554 \text{ \AA}$). The X-ray flux was $5 \times 10^{11} \text{ photons mm}^{-2} \text{ s}^{-1}$. A q range of 0.132 to $12.811 \text{ \AA}^{-1}$ was scanned, where $q = 4\pi/\lambda \sin(\theta)$ with θ being $\frac{1}{2}$ of the diffraction angle 2θ . The phase identification and volume-fraction analyses were conducted using GSAS-II.^[34] More details about this measurement can be found elsewhere.^[35] The synchrotron results were found to be within about 20 pct of the laboratory-based measurements.^[15,35] To account for as much uncertainty as possible, the uncertainty in the measured RA fraction is given as ± 20 pct of the measured value.

Samples for OM and SEM were etched with Kalling's #1 etch (225 mL ethanol, 20 mL HCl, 12 g CuCl_2) by immersion for 10 to 20 seconds, depending on the alloy

and heat treatment condition. Samples that contained more RA tended to etch faster. Energy dispersive X-ray spectroscopy (EDS) was employed, primarily in a mapping mode, to identify qualitative differences in composition between the matrix and precipitate phases, though no EDS maps are explicitly presented in the current work.

B. Computational Thermodynamics

The Thermo-Calc software package^[36] and TCFE8 thermodynamic database^[37] were used to construct multicomponent phase diagrams and for a given alloy composition and temperature to predict the equilibrium phases, their volume fractions (approximated as mole fraction), and phase compositions. The composition of the experimentally investigated alloys given in Table II were used, neglecting P and S, for calculations specific to the experiments. Additionally, representative compositions (*i.e.*, in the middle of the alloy composition specification, except C, which was set at 0.05 pct), denoted by the suffix “R” for 17-4 (17-4-R), 15-5 (15-5-R), 17-4-C (17-4-C-R), and a generic PH composition (G-PH), which encompasses composition specifications of both 17-4 and 15-5, were used for equilibrium and constrained equilibrium calculations of the alloys in general. These compositions are provided in Table III. The Thermo-Calc Parrot module and TCFE8 database were also used to calculate M_s using the model developed by Ghosh and Olson,^[38,39] described below.

C. Ghosh–Olson Model of Martensite Nucleation

Based on the theory of classical heterogeneous martensite nucleation developed by Olson and Cohen (O–C),^[40–42] Ghosh and Olson (G–O)^[38,39] used available experimental data for the FCC-to-BCC martensite transformation in Fe-based alloys to construct a model quantitatively describing the critical driving force, Δg_{chem}^c , required for spontaneous nucleation of martensite, where Δg_{chem}^c arises from the free energy difference between parent (FCC) and martensite (BCC) phases, $\Delta G_{\text{FCC} \rightarrow \text{BCC}}$. The martensite transformation is spontaneous plastic deformation driven by chemical forces. As

Table III. Compositions Used for Thermodynamic Calculations for a Representative Generic PH Stainless Steel Composition (G-PH), Representative 15-5 (15-5-R), 17-4 (17-4-R), 17-4-C (17-4-C-R) Compositions, and the Composition with the Lowest Calculated M_s Within the 17-4-C Composition Specifications (17-4-C-W)

Element	G-PH	17-4-R	15-5-R	17-4-C-R	17-4-C-W
Fe	bal.	bal.	bal.	bal.	bal.
Cr	y	16.25	14.75	16.1	16.7
Ni	4.25	4.0	4.5	4.1	4.6
Cu	3.75	4.0	3.5	3.15	3.5
Mn	0.5	0.5	0.5	0.35	0.7
Si	0.5	0.5	0.5	0.5	1.0
Nb	0.30	0.30	0.30	0.275	0.15
C	0.05	0.05	0.05	0.05	0.06
N	x	x	x	x	0.05
P	—	—	—	—	—
S	—	—	—	—	—

All compositions are given in mass fraction times 100.

such, O–C utilized the theory of dislocation slip in describing the semicoherent nucleation of martensite from a defect consisting of a configuration of multiple dislocations. Martensite nucleation occurs when the chemical driving force is sufficient to overcome the total activation energy barrier for the formation of the new phase. This activation barrier includes the defect energy and a fault energy and can be expressed as

$$-\Delta g_{\text{chem}}^c = g_{\text{el}} + \Gamma + w_{\text{ath}} + w_{\text{th}} \quad [1]$$

where g_{el} is the volume elastic strain energy associated with the martensite nucleus, Γ is the total interfacial energy between nucleus and matrix that is function of the nucleus thickness, w_{ath} is the athermal frictional work required for dislocation slip (*i.e.*, matrix/martensite interfacial motion), and w_{th} is the thermal contribution to the frictional work and is dependent on both the temperature and composition. The G–O model considered the composition dependence of this resistance to dislocation motion to be a result of solid-solution strengthening. The athermal frictional work is attributed to the long-range interactions between the elastic strain fields of the martensite nucleus interfacial dislocation array and the solute atoms. Thermal contributions to the frictional work result from short-range interactions between dislocations and solute atoms, *e.g.*, local changes in electron density or short-range order, and require thermal activation to overcome.

By assuming a fixed defect potency and converting Eq. [1] to molar quantities (where $\Delta G = V_m \Delta g$), G–O defines a critical driving force for martensitic nucleation as

$$-\Delta G_{\text{crit}} = K_1 + W_{\text{ath}} + W_{\text{th}} \quad [2]$$

G–O assumed K_1 (which contains $g_{\text{el}} + \Gamma$) as a constant, and W_{th} to become important at lower temperatures, < 500 K. Using existing solid-solution strengthening theory and available experimental data,

G–O determined K_1 , the composition and temperature-dependent quantities for W_{th} and composition-dependent quantities for W_{ath} for 14 common steel alloying elements, Al, C, Cr, Co, Cu, Mn, Mo, N, Nb, Ni, Si, Ti, V, and W. Combining their model with computational thermodynamic (Calphad) data, they demonstrated that M_s could be reasonably predicted to within ± 40 K for a wide range of alloy compositions.

III. RESULTS

A. Phase Equilibria in Precipitation-Hardenable Stainless Steels

Figure 1(a) presents an isopleth section of the phase diagram for the G-PH alloy as a function of Cr-content. The approximate delineation boundary between 17-4 and 15-5 compositions is the FCC/BCC + FCC (or FCC + MC/BCC + FCC + MC) phase boundary. At higher Cr-contents (*i.e.*, 17-4), the BCC (ferrite) phase becomes increasingly stable at elevated temperatures, and is stable at all temperatures above 18 pct Cr. The stability of BCC at higher Cr-contents produces the “ δ -ferrite stringers” typically found in wrought 17-4, whereas 15-5 contains no δ -ferrite because BCC is unstable at typical thermomechanical processing temperatures, *e.g.*, solutionization at 1323 K (1050 °C).

When 0.1 pct N is added to the system, the BCC solvus is pushed to higher Cr-contents, as shown in Figure 1(b). That is, the BCC phase becomes less stable for a given Cr composition as the N acts as an austenite stabilizer. In addition, the N addition promotes the formation of carbide, carbonitride, and nitride phases. Figure 1(b) shows that for a N-content of 0.1 pct in the G-PH composition, M_2C carbide and Z-phase are stabilized as the Cr-content increases. Z-phase is an M_2N -type nitride, known to form in Cr-containing steels that also contain Nb or V.^[43,44] Figure 2 illustrates the effects of N on phase equilibria in 17-4-R (Figures 2(a) and (c)) and 15-5-R (Figures 2(b) and (d)). The region of stability of the Z-phase has a dome shape with a maximum temperature occurring between 0.05 and 0.10 pct N. The stability and solubility range of Z-phase are highly sensitive to composition. The comparisons in Figures 2 (between (a) and (b) and between (c) and (d)) suggest Z-phase is more stable in 17-4 than 15-5. With a C-content of 0.05 pct, Z-phase is stable below temperatures of about 1323 K (1050 °C) in 17-4-R (Figure 2(a) and below 1173 K (900 °C) in 15-5-R (Figure 2(b)). However, if the C-content is decreased to 0.02 pct, Z-phase is stable to almost 1473 K (1200 °C) in 15-5-R (Figure 2(d)) and over 1473 K (1200 °C) in 17-4-R (Figure 2(c)). This implies that the Z-phase may be stable at typical thermal processing temperatures when N is present in alloys containing low concentrations of C.

Another feature of importance in Figure 2 is the gas phase boundary at high temperatures and high N-contents. The gas phase boundary is pushed toward higher N-content in 17-4-R compared to 15-5-R. This phase boundary delineates the limit of solubility of N in both

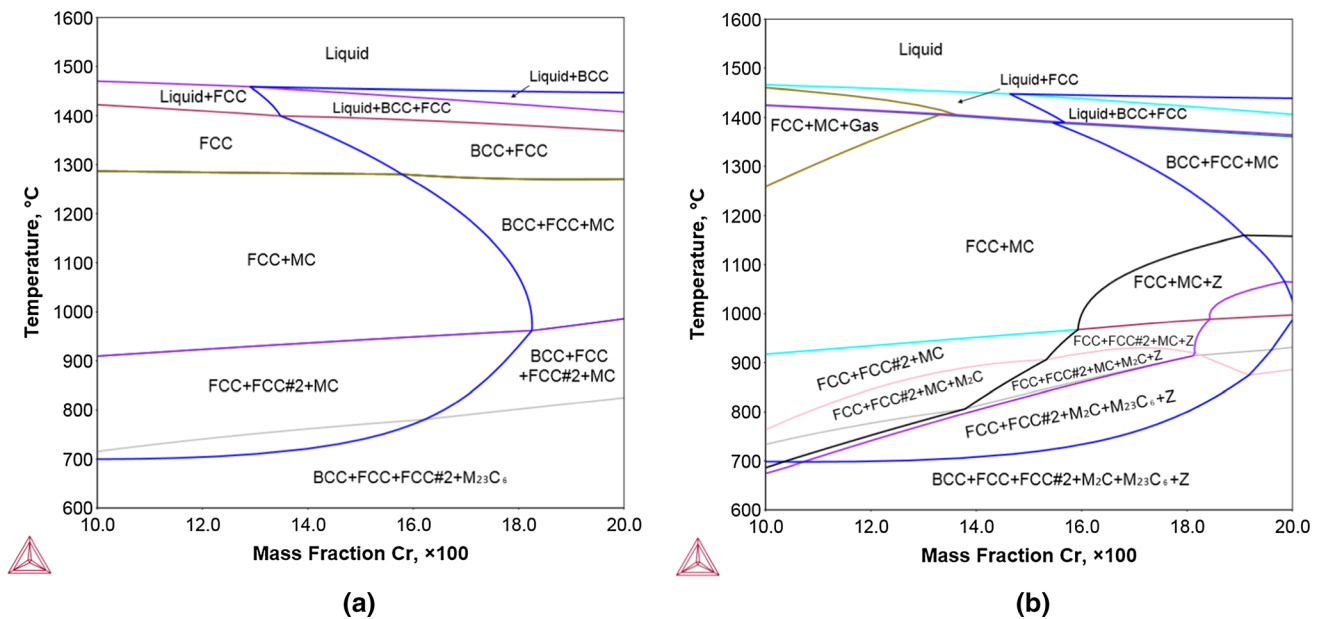


Fig. 1—(a) Isoleth phase diagrams of the G-PH alloy (xCr-4.25Ni-3.75Cu-0.5Mn-0.5Si-0.3Nb-0.05C), representative of both 15-5 and 17-4, as a function of Cr-content, and (b) the same composition as (a) except containing 0.1 pct N. FCC#2 refers to the Cu-rich FCC phase.

the liquid and solid phases and suggests the solubility of N in 17-4 is higher than in 15-5. This indicates one possible cause for the higher fractions of RA in the as-built AM 17-4 compared to AM 15-5. The presence of the gas phase at low Cr-content in Figure 1(b) also elucidates the reduced solubility of N in 15-5 (lower Cr) compared to 17-4.

B. Microstructure of AM 17-4 and AM 15-5 Compared to Wrought

Figure 3 shows optical micrographs of the microstructures in the solutionized wrought 17-4 and the as-built N₂-atomized AM 17-4, AM 15-5, and Ar-atomized AM 17-4. The microstructure of wrought 17-4, Figure 3(a), consists of almost entirely martensite with δ -ferrite stringers (thin, elongated, dark phase) scattered throughout. Wrought 15-5 (not shown) has a microstructure that looks similar to wrought 17-4, except there are no δ -ferrite stringers present. Consequently, only the microstructure of wrought 17-4 is presented here.

The microstructure of AM 17-4 shown in Figure 3(b) is similar to the wrought as a martensite matrix appears to be present throughout the image. Careful inspection of Figure 3(b) reveals faint curved lines representing melt pool boundaries and a few columnar austenite grain boundaries oriented along the build direction (both are identified in the image). In comparison, the average grain size in as-built AM 15-5 ($< 5 \mu\text{m}$), Figure 3(c), is finer than the AM 17-4 ($\approx 40 \mu\text{m}$) or wrought 17-4 ($\approx 25 \mu\text{m}$). In addition, the AM 15-5 grains also appear to be more equiaxed compared to AM 17-4. The morphology of the martensite is difficult to discern in the optical micrograph of Figure 3(c) because of the fine grain size. Melt pool boundaries are

also almost completely indistinguishable. No δ -ferrite is observed in either as-built AM 17-4 (Figure 3(b)) or AM 15-5 (Figure 3(c)).

The Ar-atomized AM 17-4 has a very different as-built microstructure, Figure 3(d), where elongated columnar grains are observed along the build direction (up in the micrograph) and appear to span several melt pool layers. The spherical dark spots in the as-built Ar-atomized AM 17-4 shown in Figure 3(d) are pores, likely resulting from the trapped insoluble Ar gas. The melt pool boundaries are decorated by small secondary phase precipitates. At present, the crystal structure of these melt pool boundary particles is unknown. No compositional variation is detected between the particles and the surrounding matrix using SEM/EDS, and XRD (not shown) reveals a nearly 100 pct BCC/martensite structure, with no detectable peaks associated with any other phase. It is also interesting to note that the columnar grains of the as-built Ar-atomized AM 17-4 in Figure 3(d) do not appear to exhibit the characteristic plate- or lath-like appearance of martensite. This is consistent with the work Alnajjar *et al.*^[45] who also observed a nearly 100 pct δ -ferrite microstructure in the as-built Ar-atomized AM 17-4; although TEM investigation is required to both identify the phases along melt pool boundaries and identify the BCC/martensite nature of the microstructure.

Figure 4 presents XRD patterns for AM 17-4 and AM 15-5 in the as-built and homogenized conditions, as well as for the solutionized wrought 17-4 (the XRD results for the Ar-atomized AM 17-4 are identical to the wrought material with no observed RA, similar to that reported by Meredith *et al.*^[8] and are not shown here). In AM 17-4, the volume fraction of RA in the as-built microstructure is extremely high, ranging from 20 pct to as high as 90 pct. Figure 4(a) shows XRD results for

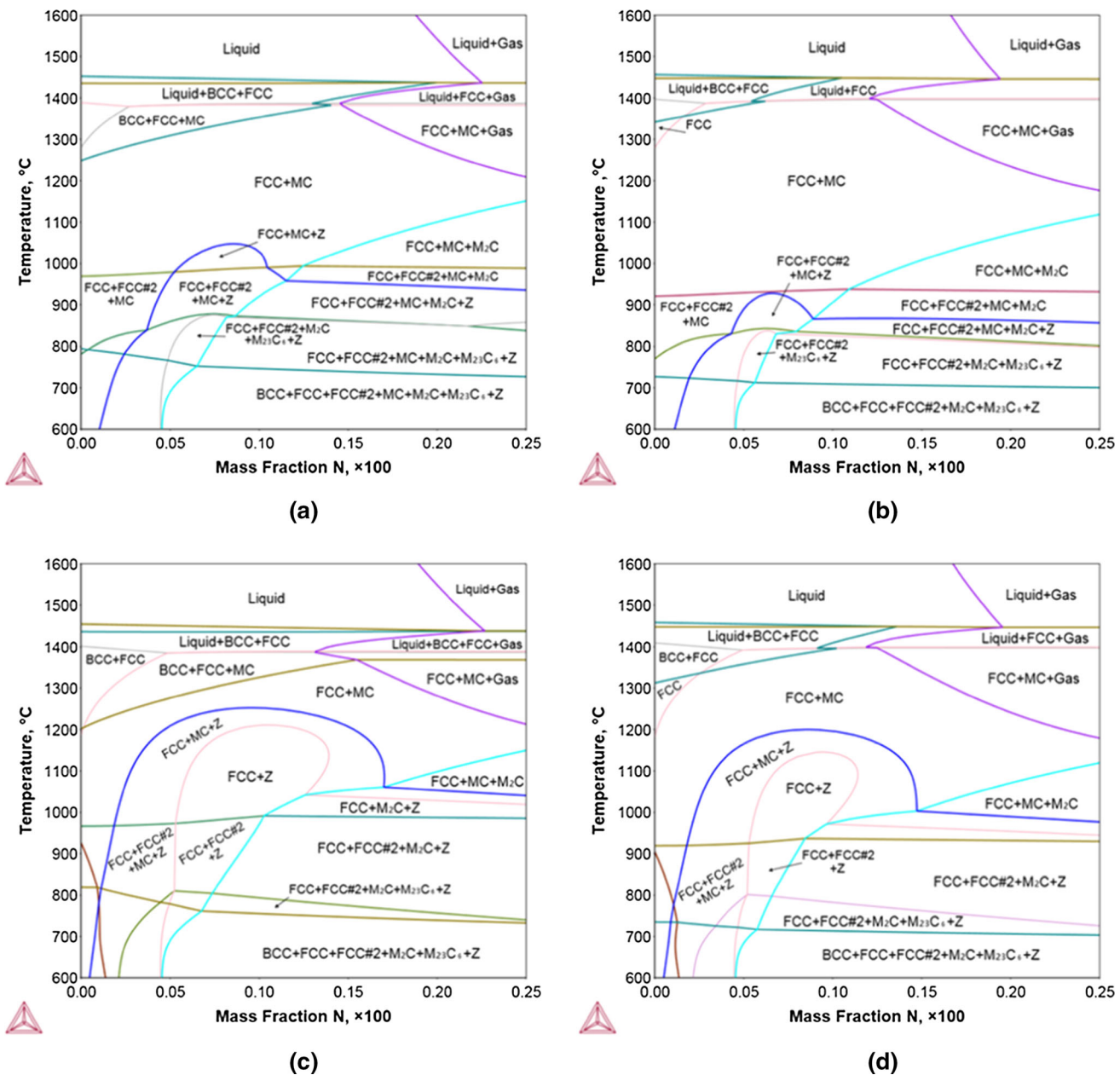


Fig. 2—Isopleth phase diagrams as a function of N-content for 17-4-R (Fe-16.25Cr-4Ni-4Cu-0.5Mn-0.5Si-0.3Nb) and a representative 15-5-R (Fe-14.75Cr-4.5Ni-3.75Cu-0.5Mn-0.5Si-0.3Nb) containing 0.05 pct C, (a) and (b), respectively, and containing 0.02 pct C, (c) and (d), respectively.

three different as-built AM 17-4 samples. The two upper samples are from the same AM build (Build A1 and A2), while the lower one is from a different build using the same lot of powder (Build B). Both A and B builds were performed on the same EOS M270 using the same processing parameters. In addition to the BCC/martensite peak, a significant FCC (111) peak exists in all three samples. Analyses of the peak intensities reveal that the RA volume fractions are (from bottom to top in Figure 4(a)) 35 pct (Build B), 26 pct (Build A1), and 55 pct (Build A2). Synchrotron XRD of a different sample from Build A determined a RA fraction of 92.2 pct, suggesting that the laboratory-based XRD-calculated RA fractions in the as-built AM 17-4 are likely too

low, a result of deformation-induced transformation of RA into martensite. The salient point of Figure 4(a) is to demonstrate that AM 17-4 built using N_2 gas-atomized powder has a large fraction of RA, considerably different than the nearly 100 pct BCC/martensite microstructure found in wrought and cast 17-4, as well as the Ar-atomized AM 17-4.

Figure 4 shows an XRD scan for the as-built AM 15-5 sample. The RA peak is quite small, with an estimated volume fraction of about 5 pct. After homogenization at 1423 K (1150 °C) for 1 hour, no discernable FCC peak is found in the XRD pattern of AM 15-5, Figure 4(c), while the homogenized AM 17-4 material still contains, about 12 pct RA. Synchrotron XRD of an

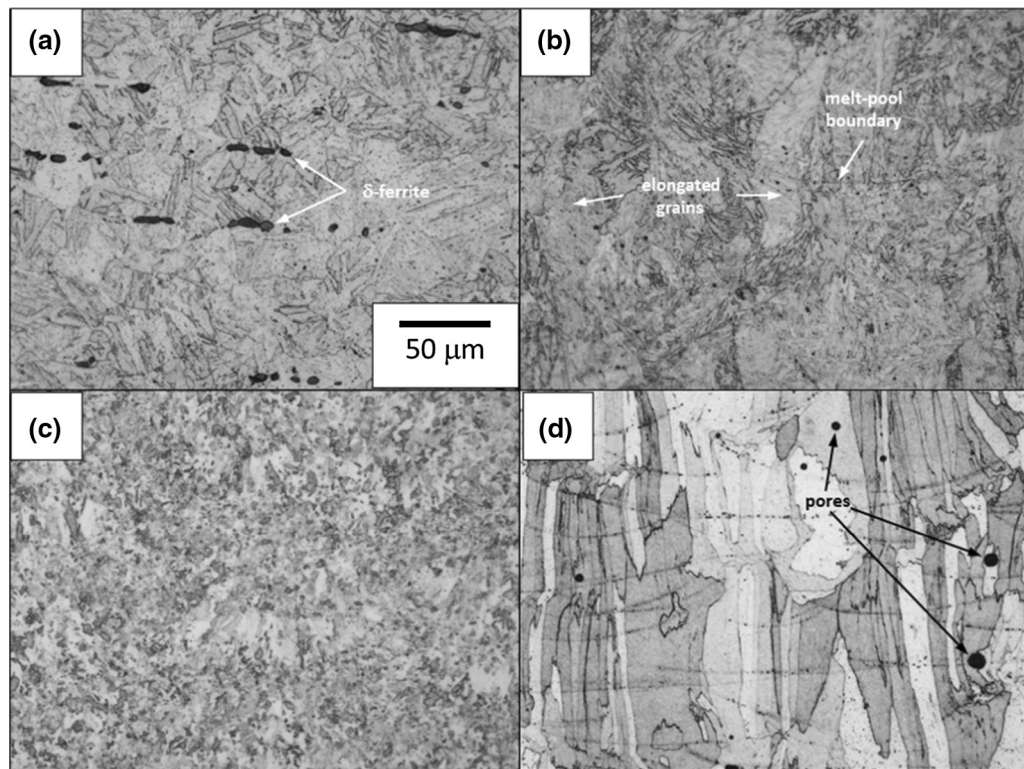


Fig. 3—Optical micrographs of (a) wrought 17-4-E, (b) as-built AM 17-4-E, (c) as-built AM 15-5-E, and (d) as-built Ar-atomized AM 17-4-E. The build direction is up in (b), (c), and (d). The scale bar is representative of all images.

AM 17-4 sample from the same build after homogenization and solutionization determined an RA fraction of 11.2 pct, very close to the laboratory-based measurement. The better agreement between laboratory- and synchrotron-based measurements in the heat-treated material is because of two reasons. First, there is less RA in the microstructure that may transform during sample preparation. Second, plastic deformation accumulates as the martensite transformation proceeds making it more difficult for the remaining austenite to transform. Both factors reduce the amount of RA that may be transformed due to the strain induced during grinding/polishing.

The AM 15-5 and AM 17-4 XRD patterns are compared to that of the solutionized wrought 17-4, shown in Figure 4(b). As mentioned above, wrought and cast 17-4 (and 15-5) alloys contain nearly 100 pct BCC/martensite, and the synchrotron measured RA fraction of the wrought 17-4 material investigated here is 1.3 pct. In this respect, the AM 15-5 material resembles wrought 15-5, and static mechanical properties are comparable as well.^[13,14,17,25–27] On the other hand, the retained austenite that remains in AM 17-4 results in dramatically different mechanical behavior including a lower yield strength, yield-point behavior, and strain-induced transformation of austenite to martensite.^[6,10,18–21]

Figure 5 presents optical micrographs of all three AM products after two post-build thermal processing heat treatments: (1) homogenization at 1423 K (1150 °C) for 1 hour followed by NBQ; and (2) homogenization then

solutionization at 1323 K (1050 °C) for 30 minutes followed by NBQ (essentially wrought/cast Condition A). All heat-treated microstructures are qualitatively similar to wrought 17-4 (Figure 3(a)). The prior austenite grains observed in all three are equiaxed, indicating that there is sufficient driving force in the as-built material, arising from either the L-PBF AM processing or the martensite transformation on cooling, or both, to facilitate recrystallization during homogenization. The L-PBF method is performed in a room temperature build chamber, which leads to large residual stresses, on the order of the materials' yield strength,^[46] that develop in the material during the cyclic heating/cooling; while the martensite transformation is essentially a phase transition that occurs through plastic deformation.

Comparing the microstructures of homogenized AM 17-4, Figure 5, and wrought 17-4, Figure 3(a), the AM 17-4 martensite structure appears to be finer, more needle- or lathe-like than the wrought, which looks more plate-like. The microstructure of the AM 17-4 material after the solutionizing heat treatment, Figure 5(b), exhibits a slightly coarser martensite, but still quite fine compared to that of the wrought 17-4. The martensite transformation on cooling from the homogenization temperature appears to impart significant plastic deformation into the microstructure, allowing the AM 17-4 to again recrystallize upon solutionizing. As the solutionization temperature is lower and the dwell time is shorter, the prior austenite grain size is smaller in the solutionized AM 17-4 compared to the homogenized material. The larger grain size in the homogenized

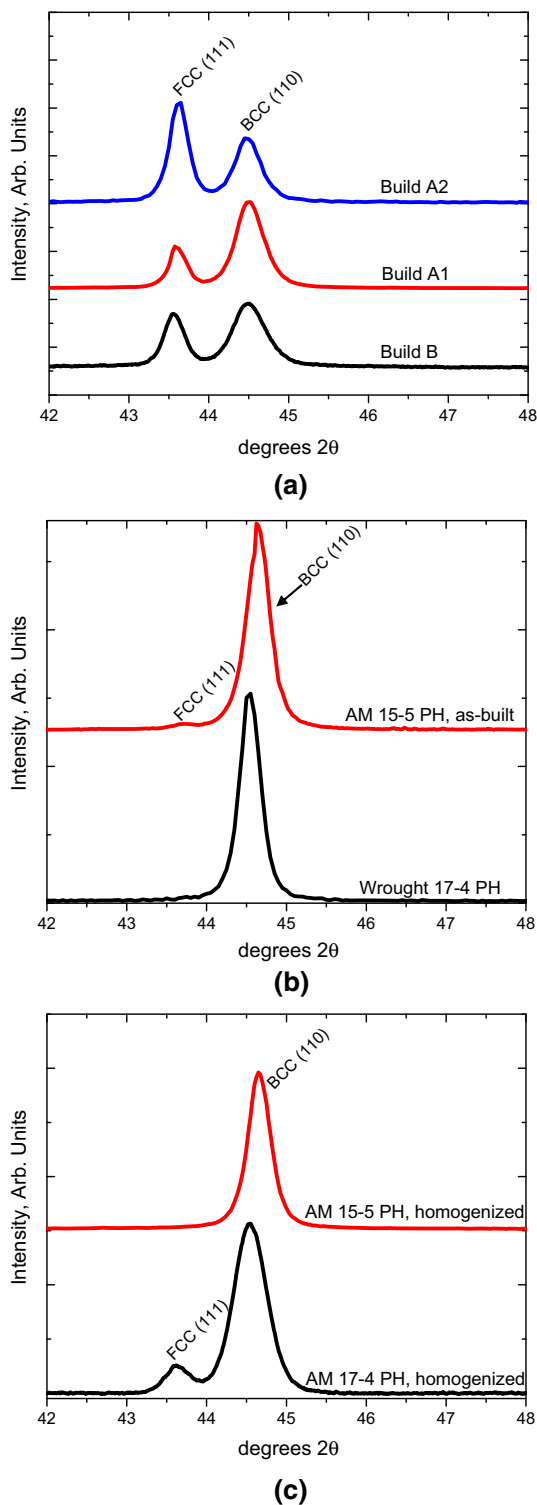


Fig. 4—(a) XRD patterns of three different as-built samples of AM 17-4-E, (b) XRD patterns of the as-built AM 15-5 and wrought 17-4, and (c) XRD patterns of AM 17-4-E and AM 15-5-E after homogenization at 1423 K (1150 °C) for 1 h.

material is more apparent in the microstructures of the AM 15-5 (Figures 5(c) and (d)) and Ar-atomized AM 17-4 (Figures 5(e) and (f)).

The microstructure of homogenized AM 15-5, Figure 5(c), is closer to wrought 17-4 than AM 17-4, with

a coarser, more plate-like, martensite structure. The prior austenite grains are smaller than the wrought 17-4, and much smaller than the homogenized AM 17-4 (Figure 5(a)). After solutionization, prior austenite grains are further refined, similar to the observed behavior of AM 17-4.

After homogenization at 1423 K (1150 °C) for 1 hour, the Ar-atomized AM 17-4 microstructure, shown in Figure 5(e) is similar to wrought 17-4, except δ -ferrite (dark phase) appears as blocky structures primarily along prior austenite grain boundaries instead of stringers as observed in wrought (Figure 3(a)). The solutionized Ar-atomized AM 17-4 shown in Figure 5(f) contains less δ -ferrite because the equilibrium volume fraction is lower at 1323 K (1050 °C) than 1423 K (1150 °C). After solutionization, the remaining δ -ferrite is no longer present along prior austenite grain boundaries due to recrystallization during solutionization. Similar to the N₂-atomized AM 17-4 and AM 15-5, the solutionized microstructure in Ar-atomized AM 17-4 also exhibits a slightly smaller prior the austenite grain size. Both the homogenized and solutionized Ar-atomized AM 17-4 still contain the large spherical pores that were present in the as-built microstructure.

Another difference between the annealed AM 17-4 and AM 15-5 microstructures compared to wrought 17-4, which is difficult to observe in Figure 5, is a much higher density of extremely fine carbides. SEM analysis of the AM 17-4 microstructure, Figure 6(a), reveals small white precipitates throughout the microstructure. There are two populations of these precipitates: (1) one population consists of coarser precipitates, approximately a few hundred nanometers in diameter that are primarily along grain boundaries (running vertically in Figure 6(a)); and (2) the second population consists of much finer precipitates, approximately 50 to 60 nm in diameter, that are distributed throughout the grain interiors. In Figure 6(a), the fine-scale precipitates are aligned in parallel rows spaced a few hundred nanometers apart (it should be noted that although this arrangement was quite common when investigating the microstructures, there were areas where this was not the case), seemingly tracking the prior solidification interdendritic regions.^[9] EDS analysis of both populations of precipitates (not shown) indicates that both forms are enriched in Nb.^[9] The phase diagrams in Figures 1 and 2 show that the MC carbide phase is in equilibrium at both the homogenization and solutionization temperatures (1423 K (1150 °C) and 1323 K (1050 °C), respectively). Indeed, MC carbides are known to form in both wrought 17-4 and 15-5, and are often utilized as grain refiners, pinning grain boundaries during recrystallization and coarsening. Therefore, both populations of precipitates in Figure 6(a) are assumed to be MC carbides. It is known that there is significant solubility of N in MC carbide, and the thermodynamic calculations suggest that N-substitution for C in MC can be 50 pct or higher, creating an M(C,N) carbonitride (which will be referred to simply as MC for convenience). Wrought 17-4 typically contains a volume fraction of MC carbides on the order of 0.1 to 0.2 pct. When N is

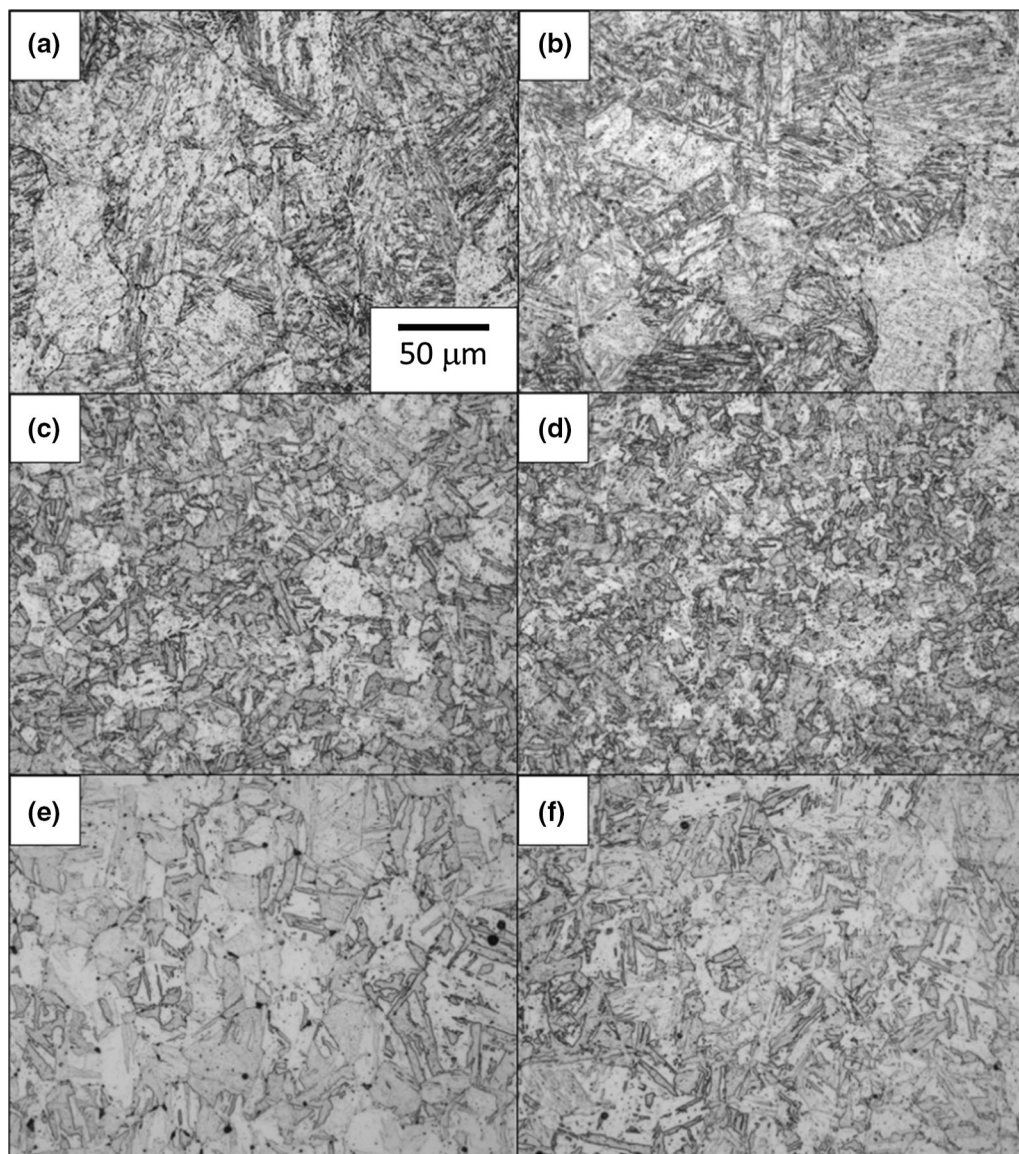


Fig. 5—Optical micrographs of AM 17-4-E after (a) homogenization (1423 K (1150 °C) for 1 h) and (b) solutionization (1323 K (1050 °C) for 30 min); of AM 15-5-E after (c) homogenization and (d) solutionization; and of Ar-atomized AM 17-4-E after (e) homogenization and (f) solutionization. The scale bar is representative of all images.

added to the system, the equilibrium MC volume fraction can increase by a factor of three or more.

The microstructure of AM 15-5 after heat treatment also contains nanoscale precipitate phases, as shown in Figure 6(b), although the precipitates are not as numerous as in AM 17-4 because the C- and N-contents are lower. EDS point analysis of the AM 15-5 precipitates also confirm that they are enriched in Nb. However, the morphology of these precipitates is more rod-like than spherical. In general, MC carbides typically have a more spherical morphology. The Cr-Nb-rich nitride Z-phase is known to form as rods in some alloys.^[43,44] M_2C carbides can also manifest as rods or faceted plates and are sometimes confused with Z-phase.^[43,44] However, the composition of the AM 15-5 material investigated in this study has a lower C-content of 0.01 pct, and Figure 2 suggests that Z-phase becomes more

stable when the C-content is low. Indeed, the calculated phase fraction as a function of temperature for the AM 15-5 composition presented in Figure 7(b) indicates that MC is in equilibrium only at temperatures between 1423 K (1150 °C) and 1673 K (1400 °C), and Z-phase is stable up to almost 1473 K (1200 °C). In contrast, the AM 17-4 material has a higher C-content, 0.05 pct, and MC is the only stable carbonitride phase between the solidus, 1623 K (1400 °C), and approximately 1323 K (1050 °C), at which temperature the M_2C carbide (also with significant solubility of N) begins to form, Figure 7(a). The Z-phase is not stable in the AM 17-4 material until below 1173 K (900 °C), even though the N-content is considerably higher than in the AM 15-5 material, 0.12 and 0.051 pct, respectively. The thermodynamic calculations and the rod-like appearance of the precipitates in AM 15-5 strongly suggest the Z-phase is

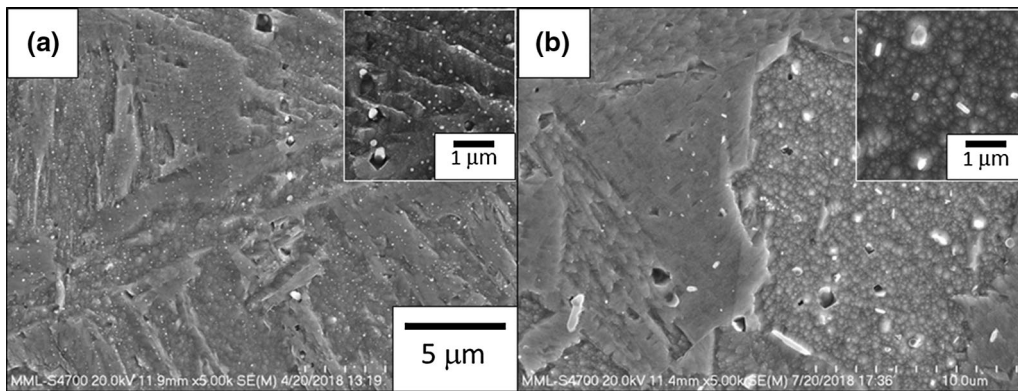


Fig. 6—SEM micrographs of (a) AM 17-4-E and (b) AM 15-5-E, after a two-stage heat treatment of first homogenizing at 1423 K (1150 °C) for 1 h and cooling to room temperature (NBQ), then solutionizing at 1323 K (1050 °C) for 30 min followed by cooling to room temperature (NBQ). The insets in each show the fine-scale carbide-(nitride) morphology in the two alloys. The larger scale bar is representative of both larger micrographs.

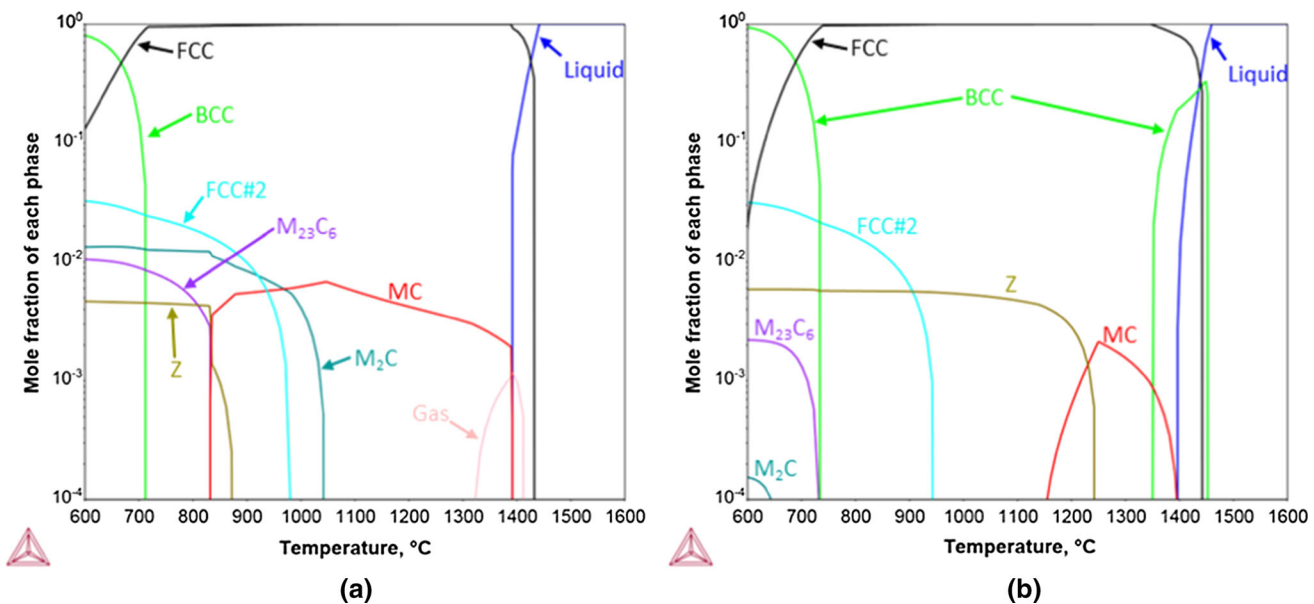


Fig. 7—Equilibrium phases as a function of temperature for the measured composition of the (a) AM 17-4-E alloy shown in Fig. 6(a), and (b) of the AM 15-5-E alloy shown in Fig. 6(b).

present. However, to determine whether these precipitates are the Z-phase, MC, M_2C , or a combination of carbonitrides requires transmission electron microscopy analysis and will be discussed in a future report.

C. The Effects of Nitrogen on the Martensite Transformation

Figure 8 shows the calculated effect of N-content on the martensite start temperature, M_s , for the equilibrium FCC matrix compositions at 1323 K (1050 °C) of 17-4-R, 15-5-R, and 17-4-C-R. 17-4-C has a specified N-concentration limit in AMS-5355, < 0.05 pct, and is included because it represents one alloy where N is expected and considered in the composition specifications. As expected, M_s decreases with increasing nominal N-content for all alloys. The M_s of 15-5-R is higher than 17-4-R for any given concentration of N. This is

primarily due to the reduced Cr-content in the alloy (in general, increasing the concentration of alloying elements in a steel reduces M_s). The cast 17-4 analog alloy, 17-4-C-R, has an even higher M_s than 15-5-R despite the higher Cr-content, because of the decreased Cu and Ni concentrations.

Also shown in Figure 8 is a horizontal dotted line at 386 K (113 °C), indicating the lowest possible calculated M_s for 17-4-C, corresponding to the composition 17-4-C-W, listed in Table III. This composition represents the “worst-case scenario,” or the extreme minimum in the M_s possible for 17-4-C, while staying within the alloy’s composition specifications. No 17-4-C alloy composition can have a calculated M_s lower than this value. If the assumptions are made that (1) the 17-4-C alloy does not have issues with too much RA within its composition specification, (2) the decrease in martensite finish temperature, M_f , is roughly equal to the decrease

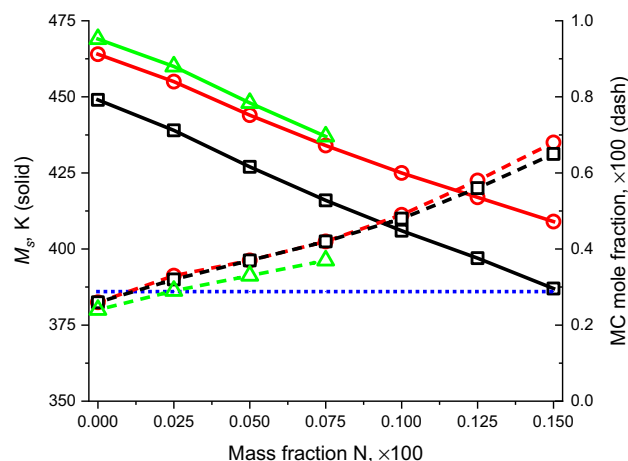


Fig. 8—The calculated M_s of the equilibrium FCC compositions at 1323 K (1050 °C) (solid) and equilibrium mole fractions of M(C,N) (dash) for 17-4-R (black-squares), 15-5-R (red-circles), and 17-4-C-R alloy (green-triangles) as a function of N-content. No other carbide/nitride phases were predicted to form at 1323 K (1050 °C) in the representative alloys for N-content up to 0.15 pct. The horizontal line represents the lowest calculated M_s for 17-4-C, the composition 17-4-C-W in Table III (Color figure online).

in M_s , and (3) the amount of RA in the final microstructure is constant for a given temperature relative to M_s and M_f regardless of the absolute values of the two temperatures, then this extremum in M_s can be used as a (rough) estimate of the critical M_s temperature required to form a fully BCC/martensite structure after solutionization (or at least a microstructure with an RA fraction below some critical level), *i.e.*, if M_s is below this threshold, an alloy may be susceptible to higher amounts of RA in the final heat-treated microstructure. Since the M_s of 17-4-R in Figure 8 is greater than this value up to 0.13 pct N, this suggests that RA would not be present (or would at least be minimal) in the final microstructure of 17-4-R. The M_s calculated for the experimentally investigated AM 17-4-E composition is 388 K (111 °C), just below this critical threshold, suggesting that if RA existed, the fraction should be small. The XRD results in Figure 4 clearly indicate a significant fraction of RA is present in the AM 17-4 microstructure, even after homogenization and solutionization, suggesting other effects may be influencing the martensite transformation in AM 17-4-E.

Figure 6 clearly identifies a population of fine-scale carbides and/or nitrides present in the microstructure of AM 17-4-E. MC-type carbides are also present in conventionally produced 17-4 material. The 17-4-R contains a calculated volume fraction of MC carbides of 0.26 pct at 1323 K (1050 °C), while the calculated equilibrium volume fraction for the AM 17-4-E composition is 0.23 pct (assuming no N in the matrix) at 1323 K (1050 °C). However, since N acts much like C, with a significant solubility in both MC and M_2C , the equilibrium carbide volume fraction increases with N-additions. With 0.12 pct N, the volume fraction of MC carbides in 17-4-R and AM 17-4-E increases to 0.55 and 0.54 pct, respectively, an increase by a factor of two.

These precipitates can act as additional barriers inhibiting dislocation motion, either through the interaction between the elastic fields of a dislocation and precipitate, or an Orowan pinning mechanism. Effects of precipitate were considered in original M_s model of Ghosh–Olson as an addition to the athermal frictional work term, W_{ath} in Eq. [2].^[38,39] However, in practice, their contribution is typically not considered because their volume fraction is low. However, the addition of N to the AM alloys dramatically increases the carbide/nitride volume fraction, and their effects on dislocation motion may not be negligible. Indeed, the precipitation of VN in N-containing CrMnNi austenitic steels has been shown to inhibit the austenite-to-martensite transformation during tensile deformation,^[47] while NbC precipitation in Fe-Mn shape memory alloys^[48] decrease the observed M_s and M_f temperatures and reduce the amount of reversible martensite. In the latter case, finer martensite plates are also observed in the NbC-containing alloy compared to the carbide-free case, which could also explain the finer-scale martensite morphology observed in the N_2 -atomized AM 17-4 compared to AM 15-5, Ar-atomized AM 17-4, and wrought 17-4. Grujicic *et al.* have considered the effects of second-phase particles on the mobility of martensite interfaces^[49] and compared their model to experimental measurements on the thermoelastic martensite transformation in Cu-Al-Ni alloys.^[50,51] It should be possible to adopt a similar approach to describe the frictional forces opposing martensite nucleation and growth arising from the carbides/nitrides in the present alloys, and then incorporate the results into the Ghosh–Olson M_s model to provide a more accurate description of martensite formation in martensitic AM stainless steels.

IV. DISCUSSION

The observed range in RA fractions from sample to sample in the as-built AM 17-4 has several possible sources, from texture in the as-built microstructure (although this was tested by rotating the samples, which resulted in no change in the measurement), powder history variation (build-to-build variation), and local processing conditions (build-to-build and sample-to-sample variation). Further variation in RA fraction can be expected when composition variation from different powder lots is considered. Other possible sources include differences in sample preparation (polishing) that change the thickness of the damage layer, which can facilitate the strain-induced austenite-to-martensite transformation. Comparison of the laboratory-based XRD results with those from synchrotron experiments suggests that such a damage layer impacts the measured RA fraction most prominently in the as-built material, likely because there is more RA that transforms into martensite during polishing. In the heat-treated samples, however, much of the austenite has already been transformed to martensite, and the remaining RA is more stable. Thus, deformation induced by sample preparation transforms a smaller

percentage of the RA. The agreement between laboratory- and synchrotron-based measurements of the annealed samples supports this hypothesis.

Regardless of the reason for the variation in measured RA in the as-built AM 17-4, significant amounts of austenite are present in the microstructure. The results clearly demonstrate that N dramatically affects the microstructure, microstructural evolution, and the martensite transformation in precipitation-hardenable martensitic stainless steels. When in solution, it decreases the thermodynamic stability of the BCC/martensite phase relative to FCC, lowering M_s and increasing the likelihood of RA in the final microstructure. When the excess N is driven out of solution by promoting the formation of carbide/nitrides, the increased volume fraction and number density of those carbides result in an additional energy barrier resisting the dislocation motion required for martensite nucleation and growth, again retarding the martensite transformation and increasing the possibility of retained austenite in the final microstructure. As the amount of N in solid solution and the type and fraction of carbides/nitrides present can be controlled by thermal processing, it may be possible to optimize the thermal processing to minimize the amount of RA in the final AM 17-4 microstructure. Indeed, Lass *et al.* recently demonstrated that a solutionization temperature of 1273 K (1000 °C) minimizes the RA level in AM 17-4 after cooling to 233 K (−40 °C), resulting in a microstructure that is ≈ 95 pct BCC/martensite.^[10] This optimized microstructure exhibits no yield-point phenomenon as found in other N₂-atomized AM 17-4 material, and the yield strength is recovered to > 90 pct of wrought 17-4.

Not only does N reduce martensite stability and promote retained austenite in a heat-treated microstructure, but if the C-concentration and other compositional variables are not carefully monitored, the type of carbide/nitride precipitates that form during post-processing can change. The Z-phase is observed in the AM 15-5-E microstructure studied here, where the bulk C and N compositions are 0.010 and 0.051 pct, respectively. According to the thermodynamic predications, Z-phase is more prone to formation in alloys with low C concentrations. Unlike MC carbides which tend to coarsen quite slowly, the Z-phase may coarsen more rapidly. This could potentially have serious consequences on mechanical properties such as fracture toughness. However, the prior austenite grain size of AM 15-5 is significantly smaller than AM 17-4. The reason for this observation is not clear from the present results, and the Z-phase may be contributing to this refined grain size.

The experimental investigation presented here demonstrates that RA found in the as-built AM 15-5 can readily be removed through thermal processing, *i.e.*, homogenization and solutionization. The reduced susceptibility to RA retention in AM 15-5 is facilitated by the higher M_s temperature (reduced Cr-content) and reduced N solubility (0.05 to 0.10 pct) compared to 17-4 (0.10 to 0.15 pct). The static mechanical properties of AM 15-5 are much closer to those of wrought 17-4 and 15-5 than AM 17-4,^[13,14,17,25–27] suggesting that 15-5

may be a more suitable candidate material for AM applications than 17-4. However, the effects of residual N on properties must be established, particularly with respect to the formation of Z-phase. Presently, there is no consensus as to whether the precipitation of Z-phase may be beneficial or detrimental to materials behavior.^[43,44] Additionally, AM 15-5 has been reported to be prone to cracking during post-build thermal processing, specifically during stress relief at 923 K (650 °C).^[13,14] One possible cause of this cracking is the high residual stresses that arise during the L-PBF build process, which could fracture the strong but brittle martensite, particularly when its strength is reduced at elevated temperatures. Therefore, a certain amount of the relatively soft, compliant austenite in the as-built microstructure, provided it can be removed *via* post-processing, may be desirable, or required, to accommodate such residual stresses and prevent cracking to allow 15-5 to be successfully utilized in AM applications, particularly laser powder-bed fusion AM where residual stresses are known to be prominent in the as-built material.

Like AM 15-5, the static mechanical behavior of Ar gas-atomized AM 17-4 is more similar to the wrought than the N₂-atomized AM 17-4.^[13,14,23,24] Similarly, the Ar gas-atomized AM 17-4 is completely or almost completely BCC/martensite in the as-built state, and thus, like AM 15-5 may also form cracks during post-build processing. Again, a small fraction of retained austenite in the as-built microstructure may be needed to prevent such cracking. However, other concerns such as cost and trapped Ar gas porosity are potential drawbacks to its use as well. The large pores found in the Ar-atomized AM 17-4 in the present study may be closed upon subsequent hot isostatic processing (HIP); however, the reopening of pores in HIP'ed material is a known issue,^[30,31] and the insoluble Ar trapped in the pores may further exacerbate this issue.

V. SUMMARY/CONCLUSIONS

Nitrogen has a dramatic effect on the microstructure and properties of additively manufactured PH-grade martensitic stainless steels, specifically 17-4 and 15-5. Nitrogen acts in a similar manner to C in steel, stabilizing FCC-austenite over BCC-ferrite and martensite. As a result, AM 17-4 built using N₂-atomized powder feedstock contains a significant fraction of RA in the as-built condition, up to 90 pct or more. AM 15-5 (N₂-atomized powder feedstock) may also contain detectable amounts of RA in the as-built state, but the fraction is significantly lower than that in AM 17-4 because of the lower solubility of N and higher martensite start temperature of 15-5 compared to 17-4. Almost no RA is found in the as-built Ar-atomized AM 17-4 material. However, the unusual microstructure of the as-built Ar-atomized materials appears to be nearly fully BCC δ -ferrite.

After post-build thermal processing, consisting of homogenization at 1423 K (1150 °C) for 1 hour and solutionization at 1323 K (1050 °C) for 30 minutes (equivalent to cast/wrought alloy “Condition A”), no

detectable RA is found in AM 15-5, and the microstructures of both AM 15-5 and Ar-atomized AM 17-4 are similar to their wrought counterparts, consisting almost completely of BCC/martensite (plus some δ -ferrite in the Ar-atomized AM 17-4). However, the homogenized and solutionized AM 17-4 material (N_2 -atomized) still contains a significant fraction of RA, between 5 and 20 pct.

The microstructure of post-processed AM 17-4 also contains a large volume fraction of M(C,N) carbides, up to three times more than that expected in wrought 17-4. Post-processing of AM 15-5 also promotes the formation of secondary carbide/nitride phases, although some of these precipitates have a different morphology, appearing more rod-like compared to the roughly spherical M(C,N) carbides found in AM 17-4. From their morphology and observed enrichment in Nb, these precipitates are presumed to be Z-phase, a Cr- and Nb-rich nitride, consistent with the calculated equilibrium for AM 15-5 at the homogenization and solutionization temperatures. Another difference between AM 17-4 and AM 15-5 is the grain size. AM 15-5 is found to exhibit a grain size nearly an order of magnitude smaller than AM 17-4 for all conditions investigated, as-built and post-processed. The reason for this observation is unclear and warrants further investigation.

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