Stable Nitride Precipitation in Additively Manufactured Nickel Superalloys

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<u>Abstract</u>

With negligible quantities of nitrogen, wrought and welded solid solution strengthened nickel superalloys usually contain carbides and topologically close-packed phases, such as Laves phase. However, appreciable nitrogen levels on the order of 0.1 % mass fraction drove the precipitation of a range of unanticipated nitride phases in additively manufactured Inconel 625 in the asdeposited and post process hot isostatically pressed conditions. Different nitride phases were observed with small changes in alloy chemistry. Cubic metal nitrides (MN), tetragonal Z-phase (CrNbN), and diamond-cubic metal η -nitrides (M₆N) were found within the γ matrix of Inconel 625 containing relatively low Fe (1 %), low Ti (0.02 %), and high Si (0.39 %) mass fractions. Conversely, these phases were replaced by only MN nitrides in a similar Inconel 625 alloy with elevated mass fractions of Ti (0.21 %) and Fe (4 %). These various phases, however, were not fully predicted using state-of-the-art computational thermodynamic tools and databases, indicating a sparsity of data for nickel superalloys. Even after hot isostatic pressing, many nitrides persisted and only experienced slight changes in composition and lattice parameters in both materials. The stability of these nitride phases presents a potential pathway for achieving enhanced high temperature and creep properties within this and similar alloy systems.

Keywords: Additive manufacturing; Nickel superalloy; Synchrotron X-ray diffraction (XRD); Transmission electron microscopy (TEM); CALPHAD

1. Introduction

With its excellent weldability and attractive high temperature and corrosion properties, Inconel 625 has become an increasingly popular alloy for additive manufacturing (AM) applications [1]. Many of its desirable properties in the wrought condition originate from solid solution strengthening and the formation of an equiaxed grain structure obtained through a series of controlled thermo-mechanical treatments. These carefully engineered microstructures are altered during welding and analogous AM processes, in which complex solidification structures containing multiple precipitates with compositional variations and irregular morphologies are formed. Slight changes in niobium and carbon compositions within the allowable specification ranges are an important factor in determining solidification sequence and phase evolution during arc welding [2-4]. Systematic variations in niobium, carbon, and, to a lesser extent, silicon compositions, changed the dominant secondary phase from MC-type metal carbides to Laves phase during arc welding [5]. Large Laves phase particles have also been shown to nucleate and grow from small carbonitrides rich in niobium and titanium [6].

AM processing is also characterized by cyclic heating, melting, solidification, and cooling conditions. In the resulting rapidly solidified microstructure, alloying elements can segregate into inter-dendritic regions and promote the formation of some secondary phases not observed in the wrought condition [7, 8]. These conditions also vary depending on the AM processing route. For example, on the one hand, high solidification velocities and temperature gradients lead to the formation of fine cellular solidification morphologies in powder bed fusion (PBF) AM processing [9-11]. On the other hand, directed energy deposition (DED) AM processing, which yield higher heat inputs similar to welding and cladding, lead to relatively coarse columnar dendritic solidification structures [3, 12]. In both cases, dendrite or cell cores are enriched in Ni, Cr, and Fe, while inter-dendritic or inter-cellular regions contain elevated levels of Nb, Mo, Si, and Ti [13].

A rather wide range of carbide and intermetallic precipitates, as summarized in Table 1, have been observed in AM fabricated Inconel 625 materials [9, 11, 14-28]. The two most common precipitates identified in as-deposited Inconel 625 are an MX-type carbonitride (M=metal, X=C,N) and a Laves phase. Both phases are enriched in Nb and preferentially located at the boundaries between grains, cells, and dendrites. In selected cases, Mo-rich η -carbides (M₆C) formed at the

expense of MX carbonitrides and Laves phase. With the addition of post-process heat treatments, these precipitates evolve, and a variety of new carbides and intermetallic compounds are observed. For example, γ " and δ phases simultaneously precipitated during stress-relief heat treatments at a temperature of 870 °C in PBF processed materials [9, 11, 29].

The presence of these different precipitates can be attributed to the combination of wide variations in composition and the preferential segregation of selected alloying elements under the rapid solidification conditions prevalent in AM processing. For example, two Inconel 625 alloys fabricated using a laser-based DED process and containing iron mass fractions of 1 % and 4 % contained secondary phases with different precipitate chemistries and located within the interdendritic regions [12, 13]. Of the various alloying elements, Nb and Mo, which increase stiffness and strength at high temperatures in these alloys, were prominent within the precipitates. Due to their solubility difference in the liquid and solid, these two alloying elements are rejected into the liquid during rapid solidification, resulting in local variations in chemical composition in as-deposited microstructures [30]. Along with titanium, they are strong carbide formers, and their enrichment in interdendritic and intercellular regions often leads to the precipitation of many of these complex carbide or nitride phases.

The evolution of these secondary phases has been primarily evaluated without considering the role of oxygen and nitrogen. While these interstitial alloying elements are not specified or typically measured [31] in wrought or cast materials, the compositions of nitrogen and oxygen in gas atomized powders commonly used in AM processing can reach levels on the order of 0.1 % [5, 7, 10, 28]. Coupled with the presence of strong nitride (Nb and Ti) and oxide formers (Al, Mn, Si, Ti) in Inconel 625, these high nitrogen and oxygen mass fractions in AM processed materials can lead to the formation of secondary phases not typically observed in wrought or welded materials.

To investigate the role of these interstitial alloying elements, two Inconel 625 materials with different levels of Fe, Ti, and Si were processed via a laser-based DED process and characterized in the as-deposited and hot isostatically pressed (HIP) conditions. The precipitates in all material conditions were analyzed at the bulk scale using transmission synchrotron X-ray diffraction and at the precipitate scale by means of high-resolution transmission electron microscopy. The experimental results are compared with predictions from computational

thermodynamic simulations to provide a link between alloy chemistry and anticipated secondary phase formation. The results presented highlight the importance of understanding the presence of interstitial elements in nickel superalloys and their effects of precipitate formation.

2. Methods

A pair of nitrogen-atomized Inconel 625 powders (Carpenter Powder Products, Inc. Reading PA¹) were used to fabricate simple wall structures using a laser-based DED AM process. One of the powders was specified to have a low Fe mass fraction (\approx 1 %) and the other a high Fe mass fraction (\approx 4 %). The walls were deposited with a 2000 W laser power, 4 mm beam diameter, 10.6 mm/s travel speed, and approximately 0.25 g/s mass flow rate. An alternating bi-directional scan strategy with a 2.29 mm to 2.54 mm hatch spacing was used for each layer, and the approximate layer thickness was 0.635 mm. Other experimental details regarding powder characteristics, equipment, build geometry, and process parameters have been reported elsewhere [12, 32] and only salient features will be discussed.

The measured chemical compositions of the powder feedstocks and AM builds met ASTM standard specifications [31] and are listed in Table 2. The nitrogen and oxygen contents, which are not required to be measured in the standard specifications, were measured using an inert gas fusion technique (ELTRA, Verder Scientific, Inc. Newtown, PA) and are also listed in Table 2. After deposition, selected builds were subjected to hot isostatic pressing (HIP) post-processing in an argon environment at a soak temperature of (1163 ± 25) °C and pressure of 101 MPa for 14400 s followed by furnace cooling to room temperature (Bodycote, Andover, MA).

Using the alloy compositions in Table 2 as input, computational thermodynamic simulations were performed using a commercially available Thermo-Calc Software TCNI8 Ni-alloys database (Thermo-Calc Software AB, Solna, Sweden) [33, 34] to probe the role of differences in the alloying element compositions on phase stability. Equilibrium calculations of phase fractions were performed as a function of temperature from (700 to 1500) °C to cover common ranges of heat treatments for Inconel 625. Solidification simulations under Scheil conditions [35] were also performed, which assume no diffusion in the solid, infinitely fast diffusion in the liquid, and

¹ Certain commercial equipment, instruments, software, or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the Department of Commerce or the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

equilibrium is reached at the solid/liquid interface at each temperature step. As a result, a composition gradient exists in the solid at the end of solidification, which is used to approximate the elemental segregation driving the subsequent precipitate formation commonly observed in asdeposited AM microstructures [36]. Carbon and nitrogen were designated as fast diffusers in the simulations, meaning their diffusion was infinitely fast in both the solid and liquid phases.

To detect and identify the secondary phases present in each Inconel 625 material, high energy synchrotron X-ray diffraction (HEXRD) was performed using beam line 11-ID-B at the Advanced Photon Source (APS) of Argonne National Laboratory (Lemont, IL, USA). High energy X-rays combined with high angular resolution were used to detect secondary phases with weak signals and accurately quantify lattice parameters not easily achieved using lower energy XRD techniques. Samples were prepared by extracting 15 mm x 15 mm cross sections along an orientation perpendicular to the build direction using a low-speed abrasive saw, followed by thinning to a 1 mm thickness using SiC grinding paper. A beam energy of 58.59 keV with a 0.2113 Å wavelength was used to obtain diffraction data over a 2 θ range from (1.0 to 11.2)° using a step size of 0.004°. The beam diameter was approximately 0.3 mm. The 2 θ peak positions were extracted from a Pseudo-Voigt fit to the data, and individual peaks were identified based on the powder diffraction files from the NIST Inorganic Crystal Structure Database [37].

The crystal structure, chemical composition, and morphology of individual precipitates were also analyzed using transmission electron microscopy (TEM). Prior to TEM sample preparation, the builds were sectioned at the mid-point of their length and mounted in an orientation which captured the full cross section of the wall height. Individual samples representing each material and processing condition were then mounted and ground using SiC grinding paper to P4000 ISO grit size, polished using 3 μ m diamond, 1 μ m diamond, and finally 0.05 μ m colloidal silica. TEM samples were prepared from selected locations in each build sample using a Scios 2 (Thermo Fisher Scientific, Waltham, US) gallium focused ion beam (FIB). After the samples were lifted out and attached to a copper grid, the samples were thinned to a thickness of approximately 50 nm using the FIB at an accelerating voltage of 30 keV followed by 5 keV final thinning methods [38].

Each sample was analyzed using a Talos F200X (Thermo Fisher Scientific, Waltham, US) TEM with an accelerating voltage of 200 kV. Both conventional TEM and high angle annular dark field scanning TEM (HAADF STEM) were used. Energy dispersive X-ray spectroscopy (EDS)

data were obtained with a superX-XEDS detector, processed using the ESPRIT software (Bruker Nano GmbH, Berlin, Germany), and elemental compositions were quantified using the Cliff-Lorimer [39] method. Gallium from the TEM sample preparation and copper from the sample grid and holder were detected in the EDS spectra but were excluded from the quantification. When microstructural features were wider than approximately 150 nm, crystallographic information was obtained using selected area diffraction (SAD) patterns with SAD aperture of 10 μ m. For microstructural features smaller that approximately 150 nm, high resolution bright field TEM images were obtained at magnifications that enable the observation of lattice fringes of the crystalline phases. Calibrated and indexed fast-Fourier transforms were processed from the lattice fringes of the crystalline phases using the Gatan GMS 3 software (AMETEK, Berwyn, US) along with the JEMS software (JEMS-SWISS, Jongny, Switzerland) to determine the crystal structures.

3. Results and Discussion

As-deposited condition

Differences in alloying element compositions can influence both the equilibrium phase stability and the partitioning of alloying elements during solidification. Since AM processing is primarily characterized by rapid solidification, the evolution of phase fractions using Scheil simulations provides a reasonable first approximation of phases present in as-deposited microstructures [7, 40]. The phase evolution during solidification approximated using Scheil simulations is plotted as a function of temperature in Figure 1 (a) and (b) for the low and high Fe Inconel 625 alloys, respectively. Nitrogen is not considered in these initial calculations, as is common when analyzing cast and wrought materials.

Aside from the appearance of small fractions of M_6C and M_2C carbides in the low Fe material, the primary FCC γ , δ , and σ phases appear in generally the same order, albeit at different temperatures for the two compositions. For example, the γ matrix phase appeared first for both materials at a temperature of approximately 1350 °C, followed by the appearance of δ and σ intermetallic phases near the terminal stages of solidification. Slight differences in the liquidus and solidus temperatures are apparent between the two compositions, with the solidus and liquidus temperatures predicted to be slightly lower in the high Fe alloy. All of these secondary phases, however, form within the final 3 % of remaining liquid during solidification, at which point the Scheil solidification calculations tend to largely overpredict elemental segregation and deviate significantly from experimental observations [41].

When nitrogen is included in the Scheil solidification calculations, significant variations in the predicted phases become apparent. In the low Fe alloy, shown in Figure 1(c), a niobium-rich MN (NbN) is predicted to form along with the γ matrix at the start of solidification. As solidification proceeds, Z-phase (NbCrN) then appears at approximately 1270 °C. In contrast, a Ti-rich MN (TiN) phase is predicted to form directly from the liquid in the high Fe alloy and is the only nitride predicted to exist across the entire solidification range, as shown in Figure 1(d). The inclusion of nitrogen in these calculations also suppressed the formation of δ and σ phase to lower temperatures corresponding to the final 1 % of liquid present at the end of solidification and eliminated the carbide phases originally predicted for the low Fe alloy.

To validate these predictions, the phases present in each as-deposited material were characterized using synchrotron HEXRD. Diffraction patterns obtained for the low Fe and high Fe Inconel 625 alloys in the as-deposited condition displayed only slight differences in appearance and are shown in Figure 2 (a) and (b), respectively. Well-defined precipitate peaks were identified in each material in the as-deposited condition. Indexing of the peaks present in the as-deposited low Fe alloy identified the presence of an FCC MN nitride ($a = (4.345 \pm 0.002)$ Å), a tetragonal Z-phase ($a = (3.072 \pm 0.001)$ Å, c = 7.532 Å), and a diamond-cubic η -nitride ($a = (11.011 \pm 0.075)$ Å). In contrast, the high Fe alloy only displayed a secondary phase with a FCC structure indicative of a MN nitride ((Ti,Nb)N, $a = (4.299 \pm 0.003)$ Å) similar to that in the low Fe material, but with a smaller lattice parameter. It was notable that only nitrides were indexed in each alloy, and no intermetallic topologically close-packed phases were identified, generally matching the Scheil solidification predictions. Although the η -nitride was observed using HEXRD, it was not predicted by simulations because the phase is not modeled to include nitrogen in the commercial database.

While the HEXRD technique can identify the presence of secondary phases, more in-depth TEM-based characterization was required to confirm the chemistry, crystal structure, and morphology of individual precipitates. In the low Fe alloy, a characteristic precipitate structure appeared in the interdendritic regions and is shown in Figure 3. The precipitate resides on a grain boundary in the FCC γ matrix and is a complex mixture of a tetragonal Z-phase with lattice parameters of $a = (3.24 \pm 0.02)$ Å and $c = (7.66 \pm 0.51)$ Å and a diamond cubic η -nitride with

lattice parameter $a = (10.95 \pm 0.05)$ Å. These precipitates, whether isolated or complex, displayed a rod-like morphology with lengths of approximately (0.5 to 1) µm. No characteristic differences in morphology were observed when comparing Z-phase and η-nitride, and MN precipitates were also observed within the interdendritic regions. As shown in Figure 4, the MN precipitate had a FCC crystal structure with lattice parameters of $a = (4.56 \pm 0.04)$ Å. Similar to the Z-phase and η-nitride, it also displayed a rod-like morphology. A summary of measured lattice parameters is given in Table 3.

In addition to being structurally distinguishable, the precipitates in the low Fe material also exhibited notable differences in chemistry, as captured qualitatively in Figure 3 and Figure 4 and quantitatively in Table 4. The MN nitride depicted in Figure 4 is dominated by Nb enrichment, reaching a mass fraction above 91 %, with corresponding depletion in all other alloying elements. Similar carbonitrides have been characterized in many nickel superalloys [3, 6, 42] and are not exclusive to Inconel 625. Within the Z-phase, the expected enrichment in Nb and Cr, as well as in Mo, was observed. Since Z-phase is generally only reported in stainless steels [43-45], a direct comparison of measured chemical compositions in other representative nickel alloys cannot be made. The high levels of Mo in the Z-phase precipitates differ from its accepted composition in stainless steels, which are rich in Nb, Cr, and V and with limited solubility of other alloying elements [44].

When compared to Z-phase, the η -nitride portion of the complex precipitate structure shows Cr depletion and enrichment in Ni and Si. The chemical composition of η -nitride (M₆N) is nearly identical to that reported for η -carbides (M₆C) characterized in welded Inconel 625 [5], with the lone difference being the replacement of carbon with nitrogen. Sometimes referred to as M₅SiN, the formation of η -nitride is promoted by the increased presence of Si in stainless steels, which is consistent with the relatively high Si composition in the low Fe alloy. High Si levels have been shown to promote the formation of η -carbides in weld metals [7, 40], and is also likely a contributing factor to the formation of η -nitrides in AM Inconel 625.

The secondary phases present in the high Fe alloy were significantly different in appearance from those observed in the low Fe alloy. Generally, the nitrides were smaller, isolated, and had more spherical or elliptical shapes with sizes less than 300 nm. As shown in the characteristic precipitate in Figure 5Error! Reference source not found., nearly all of these

nitrides contained an internal faceted oxide inclusion with a FCC crystal structure ($a = (8.24 \pm 0.05)$ Å) and composition of roughly 47 % Al, 4.5% Mg, and 48.5 % O (all in mass fraction). Oxide inclusions in AM materials have been recently found to contain combinations of amorphous, metastable, and equilibrium oxide phases [46], which can dictate morphological evolution of other primary phases. The precipitate surrounding the oxide inclusion in Figure 5 was confirmed to be an MN nitride with a FCC crystal structure ($a = (4.45 \pm 0.03)$ Å) and averaged 45.1 % Nb and 33 % Ti mass fractions over the volume of the precipitate. However, the compositions of other individual precipitates varied significantly in their Nb and Ti concentrations, with Nb/Ti ratios ranging from approximately 1.4 to 3.0.

Post-Process Hot Isostatic Pressing Condition

Post-process heat treatments and HIP processes are used with the intention of normalizing the segregated microstructures prevalent in the as-deposited materials, reducing internal porosity, and dissolving most secondary phases in nickel superalloys [47]. In this case, HIP post-processing was performed on both the low and high Fe alloys at a temperature of approximately 1160 °C. Computational thermodynamic calculations were performed to identify equilibrium phases present in this temperature range. In the absence of nitrogen, both the low and high Fe alloys, shown in Figure 6(a) and 6(b), respectively, are expected to exist as a single-phase FCC structure at the HIP processing temperature. While δ , σ , and selected carbide phases are stable at lower temperatures, their formation should be suppressed at the selected post processing temperature. Owing to differences in alloy composition, δ and σ solvus temperatures are approximately 50 °C higher in the high Fe material, while that of the MC carbide is about 100 °C lower.

When the presence of nitrogen in the material is taken into account, the predicted phase fields change dramatically, as shown in Figure 6(c) and 6(d). High temperature nitrides become stable within the liquid and persist through low temperatures in each alloy. At the post processing HIP temperature, a MN nitride exists, although the equilibrium phase fractions and compositions vary depending on initial alloy composition. For example, the MN nitride phase present in the high Fe alloy is rich in Ti, owing to the higher mass fraction of Ti (0.21 %) in the alloy. In comparison, the MN phase stable at these temperatures in the low Fe alloy is rich in Nb, since the starting alloy mass fraction is low in Ti (0.019 %). The low Fe alloy is also characterized by the presence of a stable Z-phase at temperatures near those used during HIP post processing.

These equilibrium calculations were then experimentally validated, and the phases identified in the equilibrium computational thermodynamic calculations were observed in each HIP post-processed alloy. As shown in Figure 2, multiple nitride peaks were present in HEXRD data in the HIP post-processed low and high Fe alloys. In the case of the low Fe Inconel 625, the MN nitrides present in the as-deposited condition appeared to dissolve or transform into Z-phase and η -nitride. Increases in major peak intensities coupled with the emergence of minor diffraction peaks in Figure 2(a) indicate that the Z-phase and η -nitrides are growing in the low Fe alloy. The calculated Z-phase ($a = (3.040 \pm 0.0004)$ Å, c = 7.497 Å) and η -nitride ($a = (11.02 \pm 0.018)$ Å) lattice parameters indicate slight changes from the as-deposited condition and trend closer to the tabulated values, with the Z-phase particles taking on a blocky and faceted appearance, as shown in Figure 7. Although clearly present in synchrotron HEXRD patterns, no η -nitrides were identified within the specimens prepared for TEM analysis. Only minor changes in composition of the Z-phase precipitates were observed after HIP post processing, as tabulated in Table 4, indicating that there is high temperature phase stability.

In the high Fe alloy, the phases indexed in the HEXRD patterns obtained in the HIP condition remained largely unchanged from those observed in the as-deposited material. However, the diffraction peaks corresponding to the MN precipitates shifted to higher diffraction angles, signifying changes in precipitate structure during HIP post processing. These changes in structure are connected to a decrease in the lattice parameter of MN from $a = (4.299 \pm 0.003)$ Å in the as-deposited condition to $a = (4.270 \pm 0.002)$ Å after HIP post processing. The shift in lattice parameters for the MN precipitates is driven by changes in the Nb and Ti compositions in the precipitate, with high Nb contents corresponding to larger unit cells. Since the MN peaks shifted to higher diffraction angles and smaller lattice parameters, the MN precipitates, on average, became more enriched in Ti and depleted in Nb after HIP post processing.

The evolution of the MN precipitates in the high Fe alloy after HIP post-processing is captured in Figure 8. Unlike the as-deposited condition, no oxides were present in the vicinity of MN nitrides after HIP post-processing, but the precipitate exhibited enrichment in Nb and Ti similar to that observed in the as-deposited condition, as shown in Table 4. However, the measured Ti content in the precipitate was considerably higher than the average Ti concentration in as-deposited precipitates, consistent with the HEXRD data. The nitride shown in Figure 8, for

example, was chemically complex and contained regions showing both Nb and Ti enrichment. Regardless, the Ti mass fraction in different regions of the precipitate ranged from 40.7 % to 57.7 %, which is significantly higher, on average, than the Ti mass fractions of precipitates in the asdeposited condition (33.0 %). Although within measurement error, the apparent dissolution of Nb from MN nitrides into the matrix during post-process HIP seemingly increased the average lattice parameter ($a = (3.596 \pm 0.006)$ Å) when compared to the as-deposited state ($a = (3.592 \pm 0.004)$ Å).

<u>4. Summary and Conclusions</u>

In laser-based directed energy deposition additive manufacturing of Inconel 625, alloying elements such as Fe, Ti, and Si play major roles in determining which secondary phases are present in both the as deposited and hot isostatically pressed conditions. While carbides and Laves phases are typically expected, neither of these phases was predicted by computational thermodynamics or identified in the as deposited materials. Nitrogen compositions far in excess of expected values were measured in the additively manufactured materials and originated from the gas-atomized powders. Such a high nitrogen mass fraction ($\approx 0.1 \%$) combined with varying levels of Fe, Ti, and Si drove the formation of various complex nitrides not observed in wrought, cast, or welded Inconel 625. Low Fe and Ti compositions coupled with high Si levels produced cubic MN nitrides, tetragonal Z-phase (CrNbN), and diamond-cubic η -nitrides (M₆N). In contrast, high Fe and Ti compositions led to the formation of only MN nitrides rich in Nb and Ti. After hot isostatic pressing, these various phases did undergo slight transformation, and measurable changes in composition and lattice parameters were observed. The following are major conclusions:

- High nitrogen levels present in the as deposited materials produced significant changes in the phases predicted by computational thermodynamics. In particular, the presence of MN nitrides and Z-phase with low Fe and Ti compositions and only MN phases with high Fe and Ti contents were predicted using Scheil solidification simulations.
- The presence of the predicted MN nitrides and Z-phase (CrNbN) along with η-nitrides (M₆N) in the low Fe and Ti material and MN nitrides in the high Fe and Ti material was confirmed using high energy synchrotron x-ray diffraction. High Si levels in the low Fe and Ti material likely promoted the formation of the η-nitride phase. The alloy chemistry and η-nitride phase are relatively uncommon because wrought alloys tend to have lower

nitrogen levels compared to the nitrogen atomized powder feedstocks. Due to infrequency of the η -nitride phase in Inconel® 625, it was not available in current commercial thermodynamic databases.

- Variations in the composition between the two alloys resulted in secondary phases with significantly different morphologies and compositions. For the low Fe and Ti material, the secondary phases were primarily located on grain boundaries, and the Z phase was enriched in Nb, Cr, and Mo, while the η-nitrides (M₆N) were enriched in Ni and Si. In the high Fe and Ti material, the cubic MN phase was primarily enriched in Nb and Ti.
- The chemical composition of Z-phase precipitates characterized in Inconel 625 showed significant deviations from that generally observed in similar precipitates in stainless steels. Although structurally similar, the Z-phase particles exhibited significant solubility for Mo (about 17 % to 18 % mass fraction) in Inconel 625, whereas Z-phase in stainless steels has very limited solubility for elements other than Nb, Cr, V and N.
- Hot isostatic pressing post processing of the as deposited materials produced minimal changes in the secondary phases present in the two compositions. Synchrotron X-ray diffraction results indicated that the MN nitrides present in the as-deposited low Fe Inconel 625 dissolved or transformed to additional Z-phase and η-nitride precipitates after hot isostatic pressing. Secondary phases present after hot isostatic pressing also displayed decreased lattice parameters, indicating changes in their overall composition. In particular, the high Fe and Ti material displayed an enrichment in Ti after post-processing.

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Figures



Figure 1. Comparison of the calculated phase fractions as a function of temperature during solidification under Scheil conditions when nitrogen is not included in the alloy composition for the (a) low Fe and (b) high Fe Inconel 625 and when nitrogen is included in calculations for the (c) low Fe and (d) high Fe Inconel 625. The different scales in x-axes correspond to the differences in calculated solidification temperatures.



Figure 2. Diffraction patterns acquired during HEXRD for the (a) low Fe and (b) high Fe Inconel 625 *in the as-deposited and HIP conditions.*



Figure 3. High resolution TEM image of Z-phase and η -nitride in the as-deposited low Fe Inconel 625 with corresponding FFTs and qualitative EDS composition maps.



Figure 4. High resolution TEM image of MN in the as-deposited low Fe Inconel[®] 625 with corresponding FFT and qualitative EDS composition maps.



Figure 5. High resolution TEM image of Al- and Mg- rich oxide surrounded by a MN precipitate in the as-deposited high Fe Inconel 625 with corresponding FFTs and qualitative EDS composition maps.



Figure 6. Comparison of the equilibrium phase fractions as a function of temperature when nitrogen is not included in the alloy composition for the (a) low Fe and (b) high Fe Inconel 625 and when nitrogen is included in calculations for the (c) low Fe and (d) high Fe Inconel 625.



Figure 7. TEM image of Z-phase precipitate in the low Fe Inconel[®] 625 after HIP with corresponding selected area diffraction patterns and qualitative EDS composition maps.



Figure 8. High resolution TEM image of MN precipitate in the high Fe Inconel 625 after HIP with corresponding FFT and qualitative EDS composition maps. The Ti- and Nb-rich regions of the precipitate along with the corresponding diffraction patterns are identified.

Tables

Phase	Structure	Space group	Composition	Lattice parameter(s) (Å)	
Laves	Hexagonal	$(P6_3/mmc)$	(Ni,Cr,Fe) ₂ (Nb,Mo)	a = 4.7, c = 7.7	[14-23, 27, 28]
γ'	Cubic	(Pm3m)	Ni ₃ (Al,Ti)	<i>a</i> = 3.6	[21]
γ"	Tetragonal	(I4/mmm)	Ni ₃ Nb	a = 3.6, c = 7.4	[11, 14, 18, 24]
δ	Orthorhombic	(Pmmn)	Ni ₃ Nb	<i>a</i> = 5.1, b = 4.2, <i>c</i> =4.5	[9, 11, 22]
MX	Cubic	(Fm3̄m)	(Nb,Ti)(C,N)	<i>a</i> = 4.3	[9, 18, 19, 21-26, 28]
M_6C	Cubic	(Fd3m)	(Mo,Ni,Cr,Nb) ₆ C	<i>a</i> = 11.3	[26-28]
$M_{23}C_{6}$	Cubic	(Fm3̄m)	$(Cr,Fe)_{23}C_6$	<i>a</i> = 10.8	[23, 26]

Table 1. A summary of secondary phases reported in AM Inconel 625 microstructures

Table 2. Measured mass fractions (in %) of as-deposited Inconel 625 materials and the standard specifications for wrought parts [31].

Material	Condition	Cr	Fe	Mn	Мо	Nb	Si	Ti	С	Ν	0
Low Fe	Powder	21.0	1.02	0.31	8.73	3.43	0.37	0.019	0.008	0.106	0.026
	Build	21.6	1.07	0.28	8.83	3.47	0.39	0.033	0.009	0.127	0.030
High Fe	Powder	21.3	4.34	0.010	8.70	3.83	0.035	0.19	0.005	0.105	0.006
	Build	21.5	4.14	0.085	8.96	4.11	0.051	0.21	0.006	0.080	0.007
Wrought		20 to 23	<5	< 0.5	8 to 10	3.15 to 4.15	<0.5	< 0.4	< 0.1	-	-

Table 3. Lattice parameters and measurement errors (in Å) extracted from high energy synchrotron XRD and TEM data for phases identified in the low and high Fe Inconel 625 materials.

			Lov	v Fe	High Fe			
Phase	Structure	Method	As-deposited	HIP	As-deposited	HIP		
Matrix (γ)	FCC	HEXRD	$a = 3.589 \pm 0.001$	$a = 3.586 \pm 0.002$	$a = 3.592 \pm 0.004$	$a = 3.596 \pm 0.006$		
	(Fm3̄m)	TEM	$a = 3.45 \pm 0.03$	$a = 3.44 \pm 0.02$	$a = 3.38 \pm 0.02$	$a = 3.38 \pm 0.01$		
MN	FCC	HEXRD	$a = 4.345 \pm 0.002$	-	$a = 4.299 \pm 0.003$	$a = 4.270 \pm 0.002$		
	(Fm3m)	TEM	$a = 4.56 \pm 0.04$	-	$a = 4.45 \pm 0.03$	$a = 4.56 \pm 0.06$ $a = 4.52 \pm 0.04$		
Z-phase	Tetragonal	HEXRD	$a = 3.072 \pm 0.001$ c = 7.532	$a = 3.040 \pm 0.0004$ c = 7.479	-	-		
	(P4/nmm)	TEM	$a = 3.24 \pm 0.02$ $c = 7.66 \pm 0.51$	$a = 2.90 \pm 0.01$ $c = 7.22 \pm 0.06$	-	-		
η-phase	Diamond	HEXRD	$a = 11.011 \pm 0.075$	$a = 11.02 \pm 0.018$	-	-		
	cubic (Fd3̄m)	TEM	$a = 10.95 \pm 0.05$	*	-	-		

*Not observed in TEM samples

Table 4. Elemental mass fractions (in %) from quantitative EDS measurements of individual secondary precipitates present in low and high Fe Inconel 625 materials.

Condition	Material	Phase	Cr	Мо	Nb	Ni	Si	Ti	Ν
A. 1	Low Fe	Z-phase	22.6	17.2	54.2	3.0	-	-	3.0
	Low Fe	η-nitride	12.7	15.3	35.9	32.3	2.6	-	1.2
As-deposited	Low Fe	MN	3.9	-	91.1	-	-	-	5.0
	High Fe	MN	8.6	-	45.1	-	-	33.0	13.3
HIP	Low Fe	Z-phase	22.3	17.9	55.2	0.7	-	-	4.0
	High Fe	MN (1)*	1.1	-	27.4	-	-	57.7	13.8
	High Fe	MN (2)*	3.0	-	45.2	-	-	40.7	11.1

*(1) & (2) refer to the Ti- and Nb-rich regions of MN precipitate, respectively, in Figure 8.