Influence of Hf on the heat treatment response of additively manufactured Ni-base superalloy CM247LC

Seth Griffiths a, Hossein Ghasemi-Tabasi b, Anthony De Luca a, Joanna Pado a, Shreyas S. Joglekar a, Jamasp Jhabvala b, Roland E. Logè b, Christian Leinenbach a, * a Empa - Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, 8600 Dübendorf, Switzerland
b Thermomechanical Metallurgy Laboratory, PX Group Chair, Ecole Polytechnique Fédérale de Lausanne (EPFL), 2002 Neuchâtel, Switzerland

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ABSTRACT

The influence of Hf on the heat treatment response of a Laser Powder Bed Fusion (L-PBF) fabricated Ni-base superalloy was investigated. A Hf-free version of CM247LC, CM247LC NHf, and CM247LC (~1.4 wt% Hf) were subjected to identical thermal treatments and characterized. After solutionizing at 1260 °C for 2 h, both alloys displayed recrystallization and grain growth. The CM247LC NHf had numerous annealing twins suggesting that Hf inhibits twin formation. The CM247LC NHf alloy displayed a lower peak hardness than CM247LC (5000 MPa and 5200 MPa, respectively) and this was attributed to a ~6% point reduction (Calphad calculated) in γ′-phase fraction due to the removal of Hf. Despite the lower hardness values, the CM247LC NHf displayed a higher yield strength than CM247LC at 760 °C (969 MPa and 926 MPa, respectively). Elongation at fracture at 760 °C was similar (~1%) for both CM247LC and CM247LC NHf. The removal of Hf was shown to be effective at mitigating the strain age cracking susceptibility of CM247LC, likely due to the decrease in γ′-phase fraction and lattice mismatch.

1. Introduction

Additive Manufacturing (AM), namely Powder Bed Fusion (PBF), of the L1 2-Ni3(Al,Ti, etc.) - also known as γ′ - precipitate strengthened Ni-base superalloys is especially appealing but remains a challenge due to micro-cracking. Despite the extensive investigations on the AM of γ′ strengthened Ni-base superalloys, the processing by PBF remains challenging due to the issue of extensive micro-cracking in the fabricated parts [1–9]. Three approaches are typically employed to mitigate the micro-crack issue in PBF fabricated Ni-base superalloys: (i) post-processing (ii) process modification, and (iii) alloy design.

Post-processing micro-crack mitigation is, to the authors’ knowledge, limited to healing of cracks with exposure to high pressure and high temperature, namely hot isostatic pressing (HIP). Carter et al. [1] demonstrated that post-process HIP is effective at healing internal cracks in a Laser-PBF (L-PBF) fabricated CM247LC. One key disadvantage is that surface exposed micro-cracks are not closed by HIP. Since parts fabricated by AM are intended to be near-net-shape parts, surface exposed cracks would likely exist in the final part rendering the final part unusable.

Micro-crack mitigation by process modification includes preheating, scan strategy modification, melt pool control, and laser shock peening (LSP). Ramsperger et al. [6] reported crack-free CMSX-4 samples fabricated by Electron-PBF (E-PBF) when using high fabrication temperatures (1040 °C and above). Similarly, Hagedorn et al. [10] obtained L-PBF fabricated crack-free CM247LC by preheating the baseplate to 1200 °C. Carter et al. [1] demonstrated that a simple back and forth laser scan strategy, as opposed to chess scanning, resulted in a homogenous microstructure less susceptible to crack formation. In a prior study [9] we demonstrated that the consolidation in conduction mode, as opposed to keyhole, or transition mode, results in a significant decrease in the micro-crack density. Kalentics et al. [11] demonstrated that 3D LSP applied during the L-PBF fabrication of CM247LC induced compressive residual stress which healed micro-cracks through a reverse brazing mechanism.

Crack mitigation through alloy modification has been demonstrated, but mostly in alloys with no or moderate fractions of γ′ phase. Harrison et al. [12] increased the solid-solution strengthening elements in Hastelloy X to successfully mitigate micro-cracking. Engeli et al. [13] demonstrated that the Si content of IN738LC needed to be lower than

* Corresponding author.
E-mail address: christian.leinenbach@empa.ch (C. Leinenbach).

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0.02 wt% in order to fabricate crack-free parts. In a previous study [9], we showed that a new Hf-free variant of CM247LC, CM247LC NHf, had lower susceptibility to micro-crack formation due to a reduced freezing interval. However, micro-cracking was still observed and it is clear that a realistic solution to the micro-cracking problem in PBF fabricated Ni-base superalloys will require more than just one of the aforementioned mitigation routes. For example, joint process and alloy modification further improve crack mitigation in Hf-free CM247LC consolidated parts [9].

However, consolidation by AM is only the first step in producing γ’ strengthened Ni-base superalloys parts, the γ’ precipitates need a heat treatment to nucleate and grow to optimal sizes. In conventionally cast superalloys a solutionizing heat treatment and aging treatment are required to obtain the optimal size and volume fraction of γ’. Naturally, this is a next step for AM processed superalloys, which are largely void of γ’ precipitates after printing [9]. Studies on the heat treatment and mechanical properties of PBF fabricated precipitation strengthened Ni-base alloys is somewhat limited, likely due to the aforementioned extensive micro-cracking issue [3,14,16]. Divya et al. solutionized a SLM fabricated CM247LC sample at 1230 °C for two hours and observed limited recrystallization and a grain structure similar to that observed in the as-processed condition [3]. The γ’ precipitates in both the recrystallized and unrecrystallized grains (solutionized condition) had a radius of ~100–250 nm, but the γ’ in the unrecrystallized grains had a more irregular morphology [3]. Carbides were located on the grain boundaries and were ~200–500 nm in diameter after solutionizing. Dislocation density at cell boundaries was also observed to decrease as to be expected in a solutionized sample [3]. Kunze et al. HIPed (1180 °C 4 h), solutionized (1120 °C 2 h), and aged (850 °C 20 h) a L-PBF fabricated IN738LC [14]. No recrystallization or grain coarsening was observed. The heat treated samples had a duplex γ’ precipitate size distribution of ~50 nm and ~500 nm in radius. Kanagarajah et al. solutionized (1160 °C 4 h) and aged (850 °C 16 h) L-PBF fabricated IN939 [15]. Recrystallization was observed in the heat treated samples. The γ’ precipitate radius was ~30 nm. Boswell et al. investigated the cracking occurring during the post-process thermal treatment of an AM fabricated CM247LC and attributed the cracking to both the ductility-dip and strain age cracking mechanisms [16]. A minimum in post process thermal treatment crack density was observed for samples undergoing thermal treatment at 850 °C; at this temperature, strain age cracking was identified as the primary cracking mechanism.

Room and elevated temperature mechanical properties have been reported for IN939 [15] and IN738 [14]. Few studies with high γ’ containing alloys, such as CM247LC, exist, likely due to the extensive micro-cracking observed in these alloys. Kanagarajah et al. reported room temperature and 750 °C yield strengths of ~1000 MPa (10~15% elongation) and 800 MPa (~1% elongation), respectively, for L-PBF fabricated IN939 solutionized (1160 °C 4 h) and aged (850 °C 16 h) [15]. Rickenbacker et al. performed room temperature and 850 °C tensile testing on HIPed (not reported), solutionized (1120 °C 2 h), and aged (850 °C 24 h) L-PBF fabricated IN738LC [17]. The yield strength of HIPed, solutionized, and aged IN738 in the transverse direction (gauge section perpendicular to build direction) was reported as 933 ± 8 and 610 ± 1 MPa for the room temperature and 850 °C condition, respectively. Samples parallel to build direction had slightly lower yield strengths of 786 ± 4 and 503 ± 1 MPa for the room temperature and 850 °C condition, respectively. Elongation at fracture was lower in the transverse direction than in the parallel orientation (11.2 ± 1.9% for parallel, and 8.4 ± 4.6% for transverse at room temperature; 14.2 ± 3.9% for parallel, and 8.0 ± 1.2% for transverse at 850 °C), Wang et al. [2] performed tensile testing on L-PBF fabricated CM247LC (tensile bars oriented parallel to the build direction) and observed a 792 MPa yield strength with a 6–8% elongation at fracture. Samples were not HIPed prior to testing. Kunze et al. [14] performed creep tests at 850 °C of both SLM produced samples and traditionally cast samples and found the creep rupture strength to be lower for the SLM fabricated samples. This is not completely unexpected due to the known correlation between grain size and creep properties.

While the influence of post-process heat treatment on a L-PBF fabricated CM247LC has been investigated [3,16], there are currently no studies that address versions of the alloy tailored for micro-crack mitigation, namely CM247LC NHf. Any modification to an existing alloy, even slight composition range changes, could have profound impacts on the microstructural response to heat treatment and the resulting mechanical properties, as for example a loss in ductility [9]. Here, we present an investigation of the micro-structural evolution of both CM247LC and CM247LC NHf during HIPing, solutionizing, and aging. We also present elevated temperature tensile tests of the two alloys in an attempt to address the ductility concerns.

### 2. Experimental methods

#### 2.1. Materials and additive manufacturing

Oerlikon Metco (Pfaeffikon, Switzerland) produced the inert-gas atomized powders of CM247LC as well as the Hf-free modified version, named herein CM247LC NHf. Both batches of powder had a 15–45 μm size range and a D50 of approximately 32 μm. Chemical composition of the powder was measured by inductively coupled plasma optical emission spectrometry (ICP-OES) and combustion analysis (for carbon), Table 1.

| Al | B | C | Co | Cr | Fe | Hf | Mo | Ni | Ta | Ti | W | Zr | O |
|----|---|---|----|----|----|----|----|----|----|----|----|----|----|
| 5.71 | 0.017 | 0.06 | 9.24 | 8.62 | 0.02 | 1.37 | 0.54 | Bal | 3.08 | 0.73 | 9.93 | 0.006 | 0.01 |
| 5.56 | 0.01 | 0.07 | 9.14 | 8.36 | 0.07 | 0.005 | 0.53 | Bal | 3.18 | 0.63 | 9.48 | 0.018 | 0.01 |

The consolidated samples (5 × 5 × 5 mm cubes) for the thermal treatment study and for microstructure characterization were fabricated on a Sisma MySint 100 (Sisma S.p.A., Italy), equipped with a 200 W 1070 nm fiber-laser operating in continuous wave mode with a Gaussian intensity distribution and a 55 μm spot size (1/e²). The samples were built on a 34.5 mm diameter stainless steel build plate with the following parameters: 175 W (7.35 × 10⁶ W/cm²), 750 mm/s scanning speed, 0.075 mm hatch spacing, and a 30 μm layer thickness. Samples were processed with a bidirectional scan strategy (90 degree rotation between layers) with border contour. Flowing argon shielding gas (99.996% purity) ensured the oxygen content in the build chamber did not exceed 0.1% O₂. Specimen blanks (21 × 21 × 81 mm blocks, build perpendicular to long axis) for the manufacturing of elevated temperature tensile test samples were fabricated from CM247LC and CM247LC NHf with the identical parameters listed above.

#### 2.2. Thermal treatments

Isothermal aging experiments on CM247LC and CM247LC NHf were performed in air at 850 °C on 5 × 5 × 5 mm cubes. The samples were solutionized at 1260 °C for 2 h prior to the aging experiments. All heat treatments were done independently and each stage was followed by air-cooling. Mechanical property test blanks were sent to Deloro Htm GmbH (Biel, Switzerland) for HIPing at 1225 °C and 1000 bar for 5 h. After HIPing, the specimen blanks (and witness coupons ~20 × 21 × 20 mm)
were solutionized (1260 °C 2 h) in air followed by air cooling and then aged (850 °C 8 h) in air followed by air cooling.

2.3. Characterization

Cubes and blanks for microstructure and defect characterization were sectioned (parallel to the build direction), cold-mounted in epoxy, ground, polished with monocrystalline diamond suspension and finally lapped with 50 nm colloidal silica. Samples intended for γ’ size analysis were vibro-polished with 50 nm colloidal silica and etched with V2A (200 ml H2O, 200 ml HCL 37%, 20 ml HNO3 65%) for 2 min at a temperature of 50 °C. Scanning Electron Microscope (SEM) analysis was performed with a FEI NanoSEM 230 and FEI Quanta 650 in secondary and backscatter electron imaging mode.

Microhardness measurements were performed with a Fischerscope HM2000 hardness tester with a standard Vickers diamond pyramid intender with a 136° face angle, an automated stage, and microscope. The Vickers microhardness was measured for all samples with a 1800 mN load for 60 s. Between 10 and 20 indentations were made per sample, typically in one line parallel to the build direction. No significant variation of microhardness along the build direction was observed.

Lamellae for scanning transmission electron microscopy (STEM) analysis were prepared from the aforementioned cubes (lamellae is perpendicular to build direction) using an FEI Helios NanoLab 600i focused ion beam (FIB). A FEI Titan Themis microscope, equipped with a probe spherical aberration corrector and a SuperEDX system (ChemiSTEM technology) with four silicon drift detectors for energy-dispersive X-ray (EDX) spectroscopy, was used for STEM analysis. The microscope was operated at 300 kV with a beam convergence semi-angles of 66 and 200 mrad, respectively. STEM-EDX spectrum images (with background correction) were pre-filtered.

The average size distribution of the γ’ precipitates after isothermal aging was determined via image analysis of BSE images of the aforementioned cross sections. All micrographs were taken in the center of each cubes. Image analysis was performed with ImageJ [18]. BSE images were filtered with a FFT bandpass filter, and thresholded to highlight the γ’ precipitates. Next, thresholding errors were corrected by a combination of filling holes inside of the precipitates and using a watershed tool to separate conjoined precipitates. The analysis particle feature was used to measure the equivalent γ’ precipitate size (modeled as a circle).

Density analysis of the HIPed mechanical property witness bars were performed via image analysis of 200× BSE SEM images. Carbide size and area fraction analysis of the HIPed, solutionized, and aged witness bars were performed via image analysis of 5000× BSE SEM images.

2.4. Thermodynamic simulations

Equilibrium phase fraction calculations of CM247LC and CM247LC NHf were performed with the TCNi5 database in ThermoCalc. The compositions used for the calculations are listed in Supplement Table I.

2.5. Mechanical property testing

Elevated temperature tensile testing was performed on a Gleeble 3800 machine at 760 °C (approximate minimum ductility temperature for superalloys [35]). Tensile dog-bone specimens (3 mm thick) were cut from specimen blanks via milling (profile) and wire Electro-discharge Machining (EDM) with the dimensions shown in Supplement Fig. 1.
EDM surfaces were ground with P600 paper to remove the EDM re-cast layer. In the Gleeble machine, the samples are heated by Joule effect to 760 °C at a rate of 1.5 °C/s. The samples were kept at target temperature for 2 min, and then elongated at a constant rate of 3 mm/min. The process temperature is screened with K type thermocouple welded to the surface in the middle of the samples. The testing setup and the temperature during the experiment are shown in Supplement Fig. 2.

3. Results

3.1. As-fabricated samples

Fig. 1 presents BSE images of the as-fabricated samples, CM247LC (Fig. 1a, b) and CM247LC NHf (Fig. 1c, d). In a prior study [9], we reported the density of as-fabricated CM247LC and CM247LC NHf as greater than 99.9% (measured via Archimedes method), and the microcrack density of the as-fabricated CM247LC and CM247LC NHf samples as 0.12 and 0.03 mm/mm², respectively. The as-fabricated microstructures of both alloys display a columnar grain morphology predominately oriented parallel to the build direction. The columnar grains of each alloy are composed of ~1 μm wide cells (low angle grain boundaries). In prior investigations on these alloys by Electron Backscatter Diffraction data (EBSD) [9], it was shown that the grain size (HAGB > 10°) in an as-fabricated CM247LC sample was ~40–80 μm wide and hundreds of μm in length. Both alloys contain carbides, ~55 nm in diameter and rich in Ti/Hf/Ta/W/C, located on the cell boundaries. Qualitatively, no significant difference in the carbide area fraction was observed. In-depth microstructural crystallographic and chemical characterizations of the as-printed condition of the two alloys can be found in our prior publication [9]. The as-fabricated microhardness of CM247LC and CM247LC NHf was 4337 ± 145 MPa and 4226 ± 92 MPa respectively.

3.2. Solutionized microstructure

Fig. 2 presents the microstructure of the solutionized CM247LC (Fig. 2a, b) and CM247LC NHf (Fig. 2c, d) samples. The solutionized CM247LC sample is composed of columnar grains primarily oriented parallel to the build direction and ~150–250 μm in width and ~750 μm in length. The solutionized CM247LC carbides are ~300 nm in diameter (Fig. 2b) and are typically found aligned in positions reminiscent of the original grain structure. These “walls” of vertically aligned carbides are efficient at pinning GB, or at least, slowing down the grain growth perpendicular to the build direction, potentially explaining why the columnar grain morphology remains.

In comparison, the grain microstructure of the solutionized CM247LC NHf sample appears finer and more equiaxed compared to the solutionized CM247LC. Also, numerous annealing twins are present (Fig. 2c, white arrow). Due to the slow air cooling, γ′ precipitates are formed, with mean precipitate radii of 120 and 70 nm for the CM247LC and CM247LC NHf alloys, respectively. As these precipitates are formed during cooling, a large spread in size is observed (±30 nm); the distribution, however, appears mono dispersed.

Fig. 3 presents STEM-EDX maps taken from an as-fabricated CM247LC sample (Sample from prior study [9]) (Fig. 3a) and a solutionized CM247LC sample (Fig. 3b). In the as-fabricated state, the CM247LC sample displayed significant levels of micro-segregation; Hf, Al, and Ti partitioning to the cell boundaries and W, Co, and Ni partitioning to the cell cores, with Ti-W-Ta-Hf-rich carbides detected on cell boundaries. After solutionizing, all traces of the micro-segregation have
disappeared and $\gamma/\gamma'$ phase partitioning is evident. The $\gamma$ channels are enriched in Cr, W, and Co and the $\gamma'$ cuboids are enriched in Ni, Al, Ti, Ta, and Hf. Closer STEM-EDX investigation of some of the larger $\gamma$ channels show the existence of even smaller $\gamma'$, about 25 nm radius (Supplementary Fig. 3). These precipitates represent a small fraction of the total $\gamma'$ phase and are expected to have formed in the latest stage of the slow air cooling. The number density of carbides is also strongly reduced, which correlate with their increase in sizes. Their chemistry might have also changed, as they appear to lack W. The homogenization behavior of CM247LC NHf is not anticipated to differ from CM247LC; therefore, the solutionized CM247LC NHf was not investigated.

3.3. Isothermal aging at 850 °C

The solutionizing temperature range for the Ni-base superalloys is generally limited at the upper end due to incipient melting concerns (1255 °C to 1282 °C solutionizing range for L-PBF fabricated CM247LC reported in [9]). The solutionizing temperature chosen for this study was 1260 °C, which is the same for solutionizing of conventional directionally solidified (DS) CM247LC [19]. Although removing Hf allows to significantly open the solutionizing window (1226 °C to 1341 °C), the CM247LC NHf was also solutionized at 1260 °C for comparison purposes. The solutionizing heat treatment duration was kept at 2 h, consistent with literature on DS CM247LC. Aging for DS CM247LC is typically done at 870 °C for 8 h [20]; however, a temperature of 850 °C was utilized for this study due to logistical reasons, with the 20 °C difference not expected to significantly affect precipitation kinetics.

A plot of the microhardness evolution during isothermal aging at 850 °C of CM247LC and CM247LC NHf, for durations up to 44 days, is shown in Fig. 4. The microhardness values in the as-fabricated and solutionized (1260 °C 2 h) states are added for comparison purposes. After solutionizing, the microhardness of CM247LC and CM247LC NHf was 4534 ± 92 MPa and 4575 ± 65 MPa, respectively. Upon heat treatment at 850 °C, the microhardness rapidly increases. CM247LC reaches peak hardness in 8 h, at a value of 5210 ± 104 MPa. The CM247LC NHf appears to reach peak hardness (5000 ± 115 MPa) after 2 h. At 8 h at 850 °C, the CM247LC NHf has a hardness of 4843 ± 111 MPa. For both alloys, the hardness slowly decreases at comparable rates as aging duration increases, reaching down ~4600 MPa and ~4350 MPa for the CM247LC and NHf alloys after 44 days, respectively, falling back to hardness levels comparable to the solutionized states. On average, removing Hf lead to a ~4–5% reduction in microhardness after aging heat treatment.

Fig. 3. (a) STEM-EDX map highlighting the micro-segregation of an as-fabricated CM247LC sample. Precipitates are enriched in Ti/Hf/Ta/W/C and are presumed to be carbides. (b) STEM-EDX map highlighting the homogenization (of the solidification segregation) in a solutionized CM247LC sample. The chemical analysis is performed using the Al-K, Ti-K, Cr-K, Hf-L, Ta-L, W-L, Co-K, Ni-K, Mo-K, Zr-K, and C-K lines.
presented in Fig. 5. Starting from a pre-existing population of $\gamma'$ precipitates, which results from the slow air cooling from the solutionizing temperature, it appears that, for the two alloys, the $\gamma'$ precipitates are reducing in sizes as the aging duration increases to 8 h, which corresponds to peak aging duration. At this time, the $\gamma'$ precipitates in CM247LC and CM247LC NHf have equivalent radii of $55 \pm 17$ and $34 \pm 11$ nm, respectively. BSE images of the peak aged CM247LC and CM247LC NHf samples is shown in Fig. 6. An inverse coarsening behavior (precipitates getting smaller, possibly due to cuboid splitting) is observed as duration increases to 8 h. For longer durations, the $\gamma'$ precipitates coarsen after that, with a slightly higher rate for the Hf-containing alloy. At long aging duration, the precipitates lose their cuboid shape and become initially more rounded, followed by enhanced degeneration and loss of their strength (Supplement Fig. 4 shows BSE images of 48 h aged samples). Closer inspection of the precipitate size distribution revealed that, for CM247LC, the $\gamma'$ distribution is bi-modal for durations ranging between 1 and 8 h. A comparison between the aged and solutionized distributions is provided in Supplementary Fig. 5, which allows to tentatively separate the two populations (new small precipitates vs ones formed on solutionizing) by applying a size threshold. Fig. 7a present the size evolution of the two precipitate distributions, during isothermal aging at 850°C. After 1 h of aging already, a significant fraction of $\gamma'$ with radii of ~40 nm are resolved in CM247LC (Fig. 7b). A significant reduction in radii of the large $\gamma'$ precipitates in the first 4 h is observed, while the smaller population slowly grows. At durations of 4 h and longer, the two distributions are indistinguishable and can thus be considered as one. Given the overall smaller $\gamma'$ precipitate radii observed in the CM247LC NHf samples, it is not possible to distinguish by BSE (smallest equivalent radius ~ 25 nm) the formation of an even smaller second population of $\gamma'$ precipitates. However, it is very likely that the same inverse coarsening mechanism observed in the CM247LC alloy occurs in the Hf-free version.

3.5. HIPed specimens for mechanical property testing

The microstructure of HIPed (1225°C, 5 h, 1000 bar) CM247LC and CM247LC NHf is shown in Fig. 8. No cracking was observed in the HIPed samples (lower magnification images are presented in Supplement Fig. 6). The post HIP densities (measured by image analysis) was greater than 99.9% for both the CM247LC and CM247LC NHf blanks; however, the CM247LC NHf sample did display 0.04% points more voids (highlighted by white arrows in Fig. 8). The voids appear to be unclosed lack of fusion voids. No significant grain microstructure change was observed in the HIPed CM247LC samples, aside from carbide coarsening (~55 nm
diameter as-fabricated, ~100–800 nm diameter HIPed). The grain microstructure of HIPed CM247LC NHf samples has recrystallized and numerous annealing twins are observed. Carbide coarsening was also observed in the HIPed CM247LC NHf samples (~60 nm diameter as-fabricated, ~100–900 nm diameter HIPed). Although large γ′ precipitates were observed post HIPing, since the next stage in the thermal processing was solutionizing, their size distribution was not analyzed.

The microstructure of HIPed and solutionized (1260 °C, 2 h) CM247LC and CM247LC NHf witness bars is shown in Fig. 9. Recrystallization and grain growth has occurred for the HIPed and solutionized (1260 °C, 2 h) CM247LC sample (Fig. 9 (a)). No significant difference in grain microstructure was observed between the HIPed and solutionized CM247LC NHf samples and the HIPed only CM247LC NHf samples. Cuboidal γ′ precipitates were observed in HIPed and solutionized CM247LC and CM247LC NHf samples. The γ′ precipitates (in the center of the witness bar) were ~150–200 and ~150–250 nm in radius for the CM247LC and CM247LC NHf samples, respectively; however, a detailed γ′ analysis was not performed. The carbide size (feret size) for the CM247LC and CM247LC NHf HIPed and solutionized samples is 0.44 ± 1.50 μm and 0.35 ± 0.4 μm, respectively. The HIPed and solutionized CM247LC sample appears to have rougher grain boundaries than that of the CM247LC NHf samples, but this was not quantified.

Macro-cracks (cracks hundreds of μm to mm in length) were observed on the HIPed and solutionized (1260 °C, 2 h) CM247LC witness bars (Fig. 10), but not on the CM247LC NHf witness bars. The cracking appears to be randomly oriented and intergranular (Fig. 10 (a)). The crack faces have a mostly smooth appearance (Fig. 10 (c, d)), with some small topography (small bumps) and bright particles observed (Fig. 10 (c, d)). A higher magnification image of Fig. 10 (c) is shown in Fig. 10 (e). Upon closer examination, there are line-like features (black arrow) on the bump surfaces.

The microstructure of HIPed, solutionized (1260 °C, 2 h), and aged (850 °C, 8 h) CM247LC and CM247LC NHf witness bars is shown in Fig. 11. No significant change in the grain microstructure occurred after aging. Analysis of the γ′ precipitates was not performed due to inadequate images and the small γ′ size. The carbide sizes (feret size) for the CM247LC and CM247LC NHf HIPed, solutionized, and aged samples are 0.57 ± 0.33 μm and 0.61 ± 0.35 μm, respectively. The carbide area fraction of the CM247LC and CM247LC NHf samples after HIPing, solutionizing and aging were ~1.7% and ~0.9%, respectively. Just like in the HIPed and solutionized CM247LC sample, the HIPed, solutionized, and aged CM247LC sample appears to have rougher grain boundaries than that of the CM247LC NHf samples, but this was not quantified.
3.6. Mechanical properties at 760 °C

While the Hf-free modified CM247LC alloy exhibits a reduced microhardness by ~5%, it is important to investigate other changes in mechanical properties. High temperature tensile tests were thus conducted at 760 °C using a Gleeble machine on consolidated parts from CM247LC and CM247LC NHf. The samples were HIPed, solutionized and then aged at 850 °C for 8 h (peak hardness), with the results presented in Table 2. The presented data is the average of 3 tests per alloy. The CM247LC samples displayed a 0.2% offset yield strength of 926 ± 13.3 MPa and an elongation at fracture of 1.4 ± 0.05% at 760 °C. The CM247LC NHf samples displayed a 0.2% offset yield strength of 969 ± 25.1 MPa and an elongation at fracture of 1.2 ± 0.38% at 760°C. A higher degree of elongation data scatter was observed for the CM247LC NHf alloy. One of the CM247LC NHf samples tested fractured prior to 0.2% offset yield and this sample was not included in the averaged data. Overall, the Hf-free alloy is characterized by a ~5% higher tensile strength than the base alloy, despite its lower microhardness. It however could come at the cost of slightly lower ductility, but the difference remains within standard deviation. In comparison, conventionally cast and heat treated polycrystalline CM247LC tensile tested at 760 °C by Huang and Koo [21] displayed a similar yield strength of 990 MPa but a significantly higher elongation at fracture of 7.8%. Tang et al. [22] tensile tested AM fabricated and heat treated CM247LC and obtained a yield strength of ~900 MPa and an elongation at fracture of 15%. It is important to note that in contrast to the samples tested by Tang et al., our tests were done transverse to the build direction, which is expected to have a lower ductility.

Fig. 12 displays fractography of a CM247LC sample (911 MPa yield and 1.3% elongation, Fig. 12a, b, c) and a CM247LC NHf sample (988 MPa yield and 0.73% elongation, Fig. 12d, e, f) tested to fracture at 760 °C. All fractures, on both CM247LC and CM247LC NHf samples, intersected at least one thermocouple spot weld. Overall, the CM247LC NHf samples (Fig. 12d) had a flatter, less tortuous, fracture face than the CM247LC (Fig. 12a) samples. This is most certainly related to the very different grain morphology, with CM247LC keeping a columnar grain structure post heat treatment, while grains in CM247LC NHf are more equiaxed. Both samples displayed an intergranular appearance on the fracture faces, but this appeared more pronounced on the CM247NHf samples.

4. Discussion

Significant γ′ phase precipitation was observed in the as-solutionized condition, which is contrary to what is traditionally expected after a solutionizing heat treatment. However, the Ni-base superalloys are typically highly sensitive to cooling rate from solutionizing, with the observation of γ′ phase precipitation after solutionizing being common [23]. Air cooling (no convection) was utilized for all samples, but the cooling rate was not quantified. The peak-aged condition for the isothermally (850 °C) aged CM247LC was obtained at 8 h and 2 h for CM247LC NHf; however, as there is minimal hardness difference between 2 h and 8 h for CM247LC NHf, 8 h was selected for both alloys allowing direct comparison. Inverse coarsening behavior was observed in both alloys during the first few hours of aging. This behavior has been observed in other superalloys and is attributed to elastic stresses (caused by misfits between γ and γ′) resulting in larger precipitates becoming smaller as small precipitates grow larger [24,25]. This effect will not be discussed further and the reader is directed to the references for a more thorough explanation. Most commercial γ′ strengthened superalloy
aging treatments will be at a longer duration (20 h at 870 °C for MAR-M-247, similar to CM247LC, [20]) than that observed for peak hardness. Other considerations such as optimal creep rupture strength, creep life, and fatigue life, are considered when designing heat treatments for commercial parts and these factors may necessitate coarser precipitates.

The smooth appearance of the post heat treatment crack faces, their intergranular propagation and the fact that they are observed after solutionizing of the blank samples, strongly suggest strain age cracking is occurring in the CM247LC samples, but not for CM247LC NHf. Strain age cracking susceptibility is quite high for CM247LC due to the high fractions of γ’ precipitation [26]. Strain age cracking of high γ’-fraction Ni-base alloys typically occurs during the solutionizing stage, when the part’s temperature reaches the aging temperature on its way to the set temperature [27]. Once the alloy reaches the aging temperature, the γ’ precipitation begins, which induce corresponding loss of ductility. If the residual stress present within the part is sufficiently high, then cracking occurs. Post-heat treat cracking was not observed on the cuboidal samples produced for the aging study. There are two notable differences between the samples produced for mechanical testing and those for the aging study: the samples for the mechanical property testing were (i) HIPed prior to solutionizing and (ii) of a greater section thickness. The pre-existing population of γ’ after the HIP treatment may have led to a further reduced ductility, which then increased the susceptibility to SAC when solutionizing. In addition, the greater section thickness would have provided more constraint and an increased time in the susceptible region (larger thermal mass takes longer to reach the solutionizing temperature).

Two important observations from the heat treatment study are: (i) CM247LC NHf displays a lower hardness than CM247LC; (ii) CM247LC NHf samples are not prone to strain age cracking during heat treatment. Both of these observations can be explained by the influence of Hf on the γ’ phase. Despite being widely reported as a GB strengthening element, Hf does have solubility in the γ and γ’ phases. Fig. 13(a) shows estimates of the equilibrium phase fraction of γ and γ’ phases as a function of temperature for the two alloys calculated with Thermocalc. At 850 °C, the heat treatment temperature, the equilibrium phase fraction of γ’ is 66% and 61% for the CM247LC and CM247LC NHf respectively. The 5% lower fraction of γ’ explains why the peak hardness of the CM247LC NHf is lower. It also potentially explains why the CM247LC NHf is less prone to strain age cracking, as higher fractions of γ’ phase are correlated with increased SAC susceptibility [26]. Furthermore, the lack of Hf may influence the γ-γ’ mismatch, but this was not investigated.

A lower area fraction of carbides was measured in the HIPed, solutionized, and aged CM247LC NHf sample (~0.9%) compared to the HIPed, solutionized, and aged CM247LC sample (~1.7%). In addition, a slight morphological change was observed in our prior study (Hf containing carbides in the as-solidified state are blocky) [9]. Fig. 13(b) shows an estimation of the equilibrium phase fraction of carbide, and boride phases as a function of temperature for the two alloys. Calphad calculations of the phase fraction of M6C at 850 °C for the CM247LC and CM247LC NHf were 1.4% and 0.4%, respectively (Fig. 13b). At ~600 °C, the M23C6 phase fraction is nearly identical in both alloys. It should be noted that there is a slight difference in carbon concentration between the CM247LC NHf in Thermocalc and the actual CM247LC NHf powder, and that may alter the actual phase fractions present. Interestingly, the Calphad calculations resulted in an absence of the MC phase in the CM247LC NHf alloy, but resulted in M23C6 and M6C carbides being present at intermediate temperatures, and an extended M2B temperature stability (Fig. 13b).

One aspect of Ni-base superalloy heat treatment that is only occasionally discussed in the context of AM is homogenization. Homogenization treatments are utilized for many cast alloys in order to remove the solute concentration gradients that occurred due to elemental partitioning during solidification. Micro-segregation in airfoil castings can lead to undesirable consequences such as incipient melting [20]. Directionally solidified cast Ni-base superalloys are prone to significant
micro-segregation, which is nearly identical, in terms of partition coefficient, to that observed on the L-PBF fabricated CM247LC [9]. One key difference between a directionally solidified cast part and one that is fabricated via L-PBF, is the cooling rate. The cooling rate will directly influence the spacing between areas of high and low solute concentration and thereby change the time and temperature required to completely homogenize the alloy. Zhang et al. [28] calculated the relationship between cooling rate and the primary dendrite arm spacing (PDAS) for Ni-base Superalloys and it is given by Eq. (1),

$$ PDAS = 134.43\frac{\dot{T}}{T_0^{0.26}} $$  \hspace{1cm} (1)

where \( \dot{T} \) is the cooling rate. A rough approximation of the time required to homogenize an alloy can be made with Eqs. (2) and (3)

$$ \tau = \frac{l^2}{\pi D} $$  \hspace{1cm} (2)

$$ D = D_0 e^{-Q/RT} $$  \hspace{1cm} (3)

where \( l \) is half of the PDAS, \( D \) is the diffusivity of solute at the temperature of homogenization, \( \tau \) is the relaxation time, \( T \) is the temperature of homogenization, \( Q \) is the activation energy, and \( R \) is the ideal gas constant [29]. As the cooling rate increases, the PDAS thus decreases, suggesting that the high cooling rate of the L-PBF process will result in small PDAS spacings that would then significantly reduce homogenization times per Eq. (2). Since homogenization can be quickly obtained, incipient melting during solutionizing heat treatment could be mitigated. Evidence for this is shown by the complete homogenization, disappearance of dendritic segregation, of the solutionized sample shown in Fig. 3.

The CM247LC NHf samples displayed a higher mean 0.2% offset yield stress at 760 °C than the CM247LC samples, 969 MPa and 926 MPa, respectively. In contrast, the CM247LC NHf samples displayed a lower microhardness than the CM247LC samples at RT. One potential explanation for this behavior relates to the sampling size of the microhardness measurements. The microhardness indents were ~50 μm in width. While the micro-hardness indents were sufficient to include the contribution of the \( \gamma' \) to the overall hardness, they were not of sufficient size to sample the microstructural contribution. The CM247LC NHf sample did have a slightly finer grain microstructure and the presence of annealing twins that could have resulted in the higher yield strength. It is currently unclear how Hf influences the occurrence of annealing twins, but it is clear that the absence of Hf increases their occurrence. Pande and Imam studied the influence of B on the annealing twin formation in Ni and found that 200 ppm was sufficient to suppress annealing twin formation [30]. It was hypothesized that the boron slowed the grain boundary movement thus inhibiting twin nucleation. A similar effect could take place in our system, as Hf is present on the grain boundaries. There are also expected to be differences in grain growth between the two alloys due to the morphological and composition differences of the grain boundary carbides, but this was not investigated.

Polycrystalline Ni-base superalloys show a minimum in tensile ductility between 649 °C and 871 °C and a minimum in stress-rupture ductility at ~760 °C [20]. As discussed in our prior publication [9], Hf was added to the polycrystalline superalloys in order to improve the ductility [31], specifically stress-rupture elongation. One of the
potential negative consequences of the removal of Hf could be a loss in ductility. The elongation at fracture was approximately the same for both alloys, but one of the CM247LC NHf samples tested had a low, 0.7%, elongation at fracture. As described in Section 3, all fractures intersected at least one thermocouple spot weld, which are required to control the temperature. It is therefore plausible that the welded thermocouples could have contributed to premature fracture (see Fig. 12). Furthermore, while care was taken to select CM247LC samples with no visible macro-cracks (those believed to be SAC) in the gauge section it is likely that some micro-cracks existed prior to testing. However, no evidence of fracture resulting directly from macro-cracks was observed, and the minimal spread in the data suggests the influence of cracks were minimal.

Further high temperature tensile tests with samples without spot-welded thermocouples and stress-rupture tests are required to determine if the absence of Hf will have a significant impact on the ductility and on creep elongation.

5. Conclusions

The modified alloy without Hf, CM247LC NHf, was discovered to have a few key differences from standard CM247LC in terms of heat treat response after L-PBF.

- The new CM247LC NHf alloy has lower peak hardness than the CM247LC alloy. This was attributed to the lower $\gamma'$ volume fraction.
- The new CM247LC NHf alloy appears to be less susceptible to strain age cracking. It was hypothesized that this was due to a lower $\gamma'$ volume fraction and reduced lattice misfit from the removal of Hf.
- The finer solidification structure of the L-PBF fabricated alloy will enable homogenization to occur during a standard solutionizing heat treatment.
- Annealing twins were present in CM247LC NHf after thermal treatment, but not in the CM247LC samples suggesting that Hf inhibits annealing twin formation.
- The CM247LC NHf samples displayed a higher mean 0.2% offset yield stress at 760°C than the CM247LC samples, 969 MPa and 926 MPa, respectively. The mean elongation at fracture for the CM247LC and CM247LC NHf was comparable, ~1%, suggesting that the ductility is not significantly impacted; however, spot-welded thermocouples on the samples might have induced premature failure.

### Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matchar.2020.110815.

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