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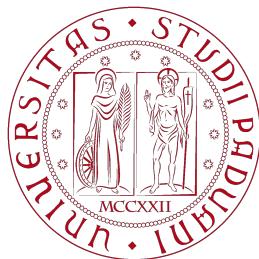
Tesi di Laurea Magistrale in Materials Engineering

**Powder Bed Fusion produced Haynes 282
Nickel-based superalloy: post deposition treatments
and long-term thermal exposure behaviour
characterization.**

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Abstract

This project focuses on the characterization of Powder Bed Fusion - Laser Beam (PBF -LB) produced Haynes 282 Nickel-based superalloy. The microstructure of samples subjected to different post-deposition treatments was analysed through X-ray diffraction, optical and electron microscopy, with emphasis on the evolution of γ' hardening precipitates and carbides.

The "CombiHIP" treatment, in which solution and two-step ageing is integrated into a single hot isostatic pressing cycle at different temperatures and holding times, made it possible to reduce the heat treatment time, improving efficiency. At the same time, it can help to reduce printing defects such as porosity and lack of fusion while reducing processing energy requirements.

Long term thermal exposure (LTTE) treatments were performed for 500 h at 760 °C, 850 °C and 930 °C to test the thermal stability of the CombiHIP processed material. Microstructural evaluation and high temperature tensile testing proved that the material held its properties after the exposure cycle at 760 °C. On the other hand, after 850 °C and 930 °C exposure, a significant coarsening of the precipitates was observed, which could have a negative effect on the mechanical properties of the material. Vickers hardness measurement validate this hypothesis, as the 760 °C exposed sample maintained pre-exposure hardness while 850 °C and 930 °C showed a 10% decay.

The results from this study indicate that PBF-LB can be used to produce high quality Haynes 282 parts, specially when combined with tailored heat treatments such as the proposed CombiHIP. LTTE cycles simulating working conditions show that the material properties remain consistent after 500 h at 760 °C, with signs of degradation at 850 °C and 930 °C.

Chapter 1

Introduction

Superalloys have been a cornerstone in the development of various industries ranging from aerospace to power generation, where the ability to work at higher temperatures leads to improvements in process efficiency. These kinds of aggressive environments require tailored material solutions, capable of holding their mechanical properties and resisting environmental damage during prolonged exposure times.

Nickel-based superalloys are the most widely spread family of high temperature materials due to their moderate cost and excellent performance. Starting on the second half of the twentieth century, the development of these alloys has seen several breakthroughs that lead to different generations of alloys outperforming their predecessors. In this context, Haynes 282 emerged as a promising wrought Ni-based superalloy with excellent balance between mechanical properties, creep resistance and processability.

At the same time, a more recent development of additive manufacturing (AM) technologies applied to the processing of metals enabled the possibility to produce intricate geometries and tailored parts of high performing materials, that are difficult or impossible to manufacture with traditional subtractive techniques. One of these techniques is laser powder bed fusion (PBF-LB), in which parts are constructed layer by layer from a 3D model as material powder is selectively melted by a laser.

The combination of the high performance of superalloys with the versatility of additive manufacturing offers a great opportunity for taking the innovation in these key industries one level further, producing small batches of specific components that were impossible to manufacture some decades ago.

Several studies exist on the additive manufacturing of superalloys, including the aforementioned Haynes 282. However, the combination of the complex chemical composition and microstructure of this material with the severe thermal gradients, rapid cooling rates and dynamics of the printing process, leads to several metallurgical challenges. Porosity, segregation, microcracks and anisotropy has been observed in the as-built condition for PBF-LB produced Haynes 282. Overcoming these problems is critical to produce standard compliant high quality parts for demanding industries.

For this reason, post-processing of the material is often required, including high-temperature and high-pressure treatments such as Hot Isostatic Pressing (HIP). In this project, the utilization of HIP is evaluated as a way to combine multiple treatment steps into one, aiming to reduce processing time and energetic costs.

In view of this, the objective of this project is to investigate the influence of different post-processing routes combined with HIP of PBF-LB produced Haynes 282 superalloy, with emphasis on its microstructural evolution and the effect on the mechanical properties at the operation temperatures.

Microstructural characterization in the different conditions will include different techniques such as light optical microscopy (LOM), scanning electron microscopy (SEM) and x-ray diffraction (XRD). After defining thermal exposure treatments based on literature review, the exposed specimens will be subjected to high temperature tensile testing for the determination of their mechanical properties and fracture analysis.

The relevance of this work lies in the importance of an integral and deep understanding of the effects of processing conditions in the properties of the material, not only right after it has been produced but also after being in service. For example, the loss of ductility and strength, and their root in microstructural instabilities needs to be quantified to ensure the integrity of critical components during their complete expected working life.

Chapter 2

Theoretical background

2.1 Nickel-based superalloys

Superalloys emerged in the second half of the twentieth century as a superior alternative for high temperature applications. High temperature materials need to be able to withstand loading at operating temperatures close to their melting point, resist mechanical degradation over extended periods of time and tolerate aggressive environments [1]. These characteristics are desirable in different fields, including jet engines and ultra-supercritical thermal power plants, where a higher operating temperature leads to an improvement in the efficiency of the processes.

The use of nickel as the most spread matrix for superalloys responds to different reasons: first, it is abundant in the earth crust and thus has a moderate cost. Second, it has a face centred cubic (FCC) crystalline structure that is stable from room temperature up to its melting point, avoiding phase transformations that may cause undesirable strains. Moreover, FCC materials are characterized by their toughness and ductility, which results from their multiple slipping planes. Lastly, it has a low self diffusion rate, which is beneficial to retard thermally activated creep [1]. Even though Ni-based superalloys are the most popular ones, other available compositions use cobalt as the main element, which shares the advantages of nickel for these applications but comes at a higher cost.

The term nickel-based superalloys corresponds to a group of materials that contain numerous alloying elements in variable and relatively high concentrations. These can be classified according to their interaction with the Ni matrix. Elements with atomic radii similar to Ni such as cobalt, iron, chromium, molybdenum and tungsten partition to the austenitic matrix, stabilizing it. A second group, including aluminium, titanium, niobium and tantalum have a slightly greater atomic radius and promote the formation of ordered phases known as γ' . Lastly, boron, carbon, zirconium, molybdenum niobium and titanium are also carbide and boride formers, which partly segregate to the grain boundaries [1].

As a result of the wide variety of alloying elements, the microstructure of different superalloys can show significant differences in the presence or absence of phases, their

morphology, and proportions. Nonetheless, the typical Ni-based superalloy microstructure usually consists of:

- Gamma phase (γ): Continuous FCC matrix. It contains the previously mentioned γ stabilizers in solid solution. An initial estimation of an element capacity to stay in solid solution can be made with the Hume-Rothery rules that state that substitutional solid solution is likely to take place if the atomic radii, crystalline structures, valence and electronegativity are similar among the species [2]. However, it is important to notice that these rules apply only to binary mixtures and the interaction between multiple components is more complex, and usually modelled through thermodynamic simulations.
- Gamma prime precipitates (γ'): Discontinuous FCC precipitates, often coherent with the γ matrix. The base composition of this phase is Ni_3Al , an intermetallic compound that exhibits directional covalent bonding which results in an ordered structure, shown in Figure 2.1. Each element has a distinct site occupation: the aluminium atoms occupy the cube corners and the nickel ones the centres of the faces. Substitutional elements in the lattice usually replace Al if they are bigger (Ti, Ta) and Ni if they are smaller (Co), but rarely show mixed behaviour [1].
- Carbides and borides: Carbon combines with reactive elements to form primary MC carbides during solidification. During posterior heat treatments, secondary carbides of the form $M_{23}C_6$ and M_6C may also precipitate both within the grains and in grain boundaries. On a similar manner, boron combines with molybdenum and chromium to form M_3B_2 borides, in smaller proportions.

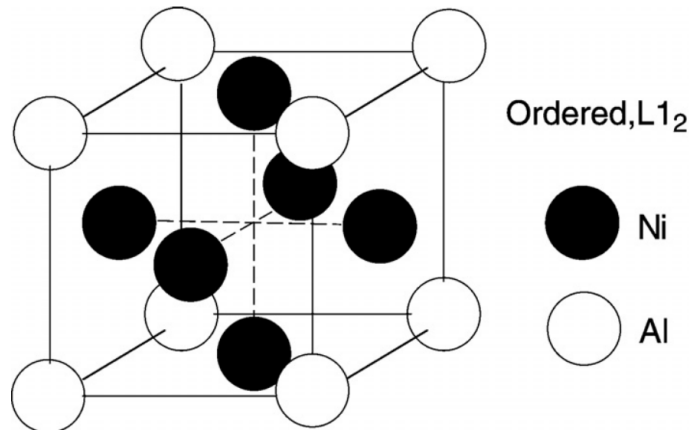


Figure 2.1: Atomic distribution in the Ni_3Al phase [1].

Other phases that might be present in some superalloys microstructures are:

- Gamma double prime precipitates (γ''): Intermetallic compounds of the form Ni_3Nb which are the primary strengthening precipitate in some nickel-iron superalloys. They have a body-centred tetragonal (BCT) structure and often display a disc morphology.

They are generally coherent with the matrix but have higher coherency strain than γ' .

- Topologically close-packed (TCP) phases (μ , σ , Laves): These compounds of the form A_xB_y , where A and B are transition metals, have very wide stoichiometry ranges and different crystalline structures. Their common characteristics are their high packing density, directional bonding and stacked polyhedra structure [1]. As a result, they are usually brittle and thus undesirable.

Another important factor influencing the microstructure and properties of Ni-based superalloys is the relationship between phases. In particular the lattice misfit between γ and γ' , which is dictated by the solutes partitioning, has a critical effect on the morphology of the precipitates. As precipitate development occurs, their morphology goes from spheres, to cubes, cuboidal arrays and finally, solid state dendrites. The size at which these transitions take place was found to be proportional to the lattice misfit [3]. A small misfit also results in a coherent γ/γ' interface with low interfacial energy, which is beneficial for the properties of the material [1].

The presence or absence, quantity, morphology and composition of these phases depends not only on the chemical composition of the alloy but also on their thermomechanical history. For example, TCP phases may be observed after long term thermal exposure (LTTE) and γ' precipitation may be suppressed through quenching. For this reason, thermomechanical treatments need to be understood to comprehend the behaviour and microstructure of superalloys.

Heat treatments are specific to each alloy and tailored for specific applications. Nonetheless, they usually consist of two distinct stages. The first one, solutioning, is carried out at a temperature above the solvus temperature of both γ' and secondary carbides. After these phases are dissolved, the material needs to be cooled down quickly enough to avoid re precipitation (quenching). Then, during the ageing treatment, that can be done in one or multiple steps, the alloy is reheated to promote controlled precipitation both of carbides and γ' [4]. Holding time and temperature are crucial in these steps to obtain a discrete precipitation of grain boundary carbides that helps to control grain size and improve creep resistance; and uniformly distributed γ' precipitates that contribute to the alloy's strength by precipitation hardening [4].

It is important to notice that γ' hardened superalloys exhibit a so-called anomalous yielding effect: an increase in the yield strength with temperature up to 800 °C. This phenomenon is partly attributed to the thermally activated cross-slip of dislocations from octahedral to cube planes in the γ' precipitates, that results in the formation of anti-phase boundaries that act as microstructural locks (Kear-Wilsdorf locks [5]), resisting deformation [1]. At even higher temperatures, the slipping mechanism changes again, leading to a rapid decrease in the tensile strength.

2.1.1 Haynes 282

As mentioned before, the term superalloy encompasses a very broad family of materials. The particular alloy concerning this project is Haynes 282. This material is a wrought, γ' strengthened superalloy, developed with the objective of achieving a good balance between processability and strength [6]. This combination of good mechanical properties with the good formability and weldability make this alloy suitable for applications such as aircraft engines, advanced ultra-supercritical steam turbines and marine offshore energy systems [7].

Its nominal chemical composition can be seen in table 2.1. Every element contributes in one or more ways to the alloy performance. For example, Cr ensures oxidation resistance by forming a Cr_2O_3 protective layer, Mo increases creep strength, and Ti and Al create strengthening γ' precipitates [7]. A complete description of the different roles from alloying elements is shown in Table 2.2.

Table 2.1: Chemical composition of Haynes 282 [6].

Element	Ni	Cr	Co	Mo	Ti	Al	Fe	Mn	Si	C	B
Weight %	Bal.	20	10	8.5	2.1	1.5	1.5 max.	0.3 max.	0.15 max.	0.06	0.005

Table 2.2: Alloying element effects on Ni-based superalloys. Not all these phenomena necessarily occur in a given alloy. Adapted from [8].

Effect	Alloying element
Solid-solution strengtheners	Co, Cr, Fe, Mo, W, Ta, Re
Carbide form: MC	W, Ta, Ti, Mo, Nb, Hf
Carbide form: M_2C_3	Cr
Carbide form: $M_{23}C_6$	Cr
Carbide form: M_6C	Mo, W, Nb
Carbonitrides: $M(CN)$	C, N
Forms γ' $Ni_3(Al, Ti)$	Al, Ni, Ti
Raises solvus temperature of γ'	Co
Hardening precipitates and/or intermetallics	Al, Ti, Nb
Oxidation resistance	Al, Cr, Y, La, Ce
Improve hot corrosion resistance	La, Th
Sulfidation resistance	Cr, Co, Si
Improves creep properties	B, Ta
Increases rupture strength	B
Grain-boundary refiners	B, C, Zr, Hf
Retard γ' coarsening	Re

In comparison to other similar performance alloys, Haynes 282 relatively low aluminium and titanium content results in a lower γ' fraction which leads to an improvement in fabricability and reduces the risk of strain age cracking. Strain age cracking affects welded components and is associated with residual stresses caused by solidification shrinkage and γ' formation during post weld heat treatments [9]. The low γ' content in Haynes 282 and more sluggish precipitation kinetics help to mitigate this problem [10]. At the same time,

the relatively high Mo content contributes to the thermal stability of the alloy, and was experimentally tailored to maximize creep resistance [10].

According to the manufacturer, the alloy is provided in a solution-annealed condition, which is achieved through a heat treatment in the range from 1121 to 1149 °C. The recommended standard heat treatment consists of a two-step ageing, the first one to be carried out at 1010 °C for 2 hours followed by air cooling, and the second one at 788 °C for 8 hours, also followed by air cooling [6].

In the age-hardened condition the material achieves a 1% creep strength at 760 °C of 345 MPa for 100 h and 248 MPa for 1000 h. At room temperature (RT), a tensile yield strength (TYS) of 715 MPa, ultimate tensile strength (UTS) of 1147 MPa and elongation of 30% [6]. Regarding its high temperature mechanical resistance, the alloy retains most of its RT strength up to 600 °C, which then starts a slow decline between 600 and 760 °C, after which a stronger deterioration takes place [11].

This behaviour can be related to the micro-mechanism controlling plastic deformation. As it is shown in Figure 2.2, below 600 °C, deformation is controlled by shearing of γ' precipitates by Anti Phase Boundary (APB) coupled dislocations. The critical shear stress associated to this process depends on the microstructure and the APB energy, which remain almost constant with temperature up to 600 °C. As a result, the yield strength holds its value in this range, with the slow decline afterwards mostly related to the strength of the matrix and grain boundaries. At higher temperature the controlling mechanisms change to stacking fault shearing and Orowan looping, the critical shear stress is lower, and its dependence with temperature stronger, which in turn results in a faster decay of the mechanical strength of the material [11].

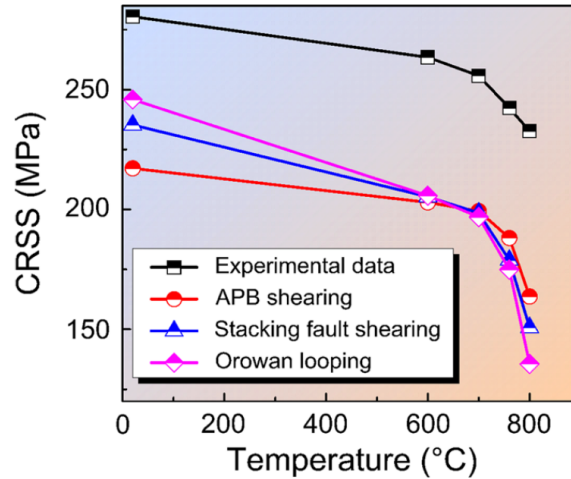


Figure 2.2: Experimental and calculated critical shear stresses as a function of temperature for Haynes 282 [11].

The simulated equilibrium phase diagram for this alloy is shown in Figure 2.3. The complexity of the chemical composition derives in multiple phases coexisting. Moreover, due to kinetic limitations, the non equilibrium microstructure might differ significantly from what is expected according to the phase diagram. For example, in heat-treated

wrought products γ , γ' and carbides are usually the only phases present [12]. In contrast, σ TCP phase, TiN and carbosulphides have also been reported in cast products [13].

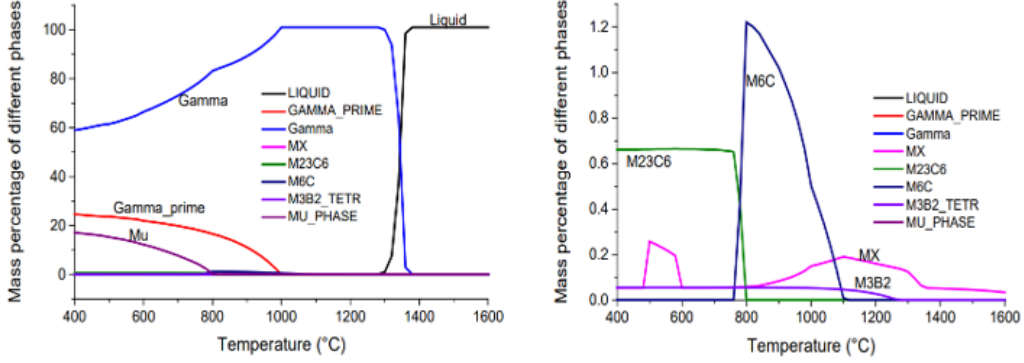
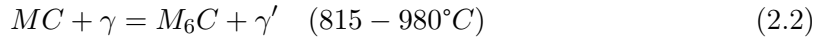
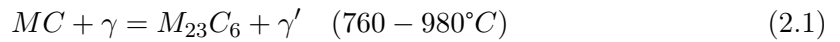


Figure 2.3: Haynes 282 equilibrium phase diagram [14].

Scheil solidification calculations can be more accurate to simulate the solidification process in non equilibrium conditions. In this model, it is assumed that there is homogeneous distribution of solute elements in the liquid and no diffusion in the solid. This can resemble high cooling rate conditions [15] such as the ones found in welding or additive manufacturing processes.

Upon thermal exposure, primary carbides may decompose into secondary carbides according to the Equations 2.1 and 2.2 [13]. Following this observation, Fahrmann et al. developed a Time-Temperature-Transformation (TTT) diagram for this alloy, starting from the mill annealed condition and exposing samples to different combinations of time and temperature. The resulting diagram, shown in Figure 2.4 highlights the faster precipitation kinetics of $M_{23}C_6$ compared to M_6C and a solvus temperature for both around 1120 °C [12].



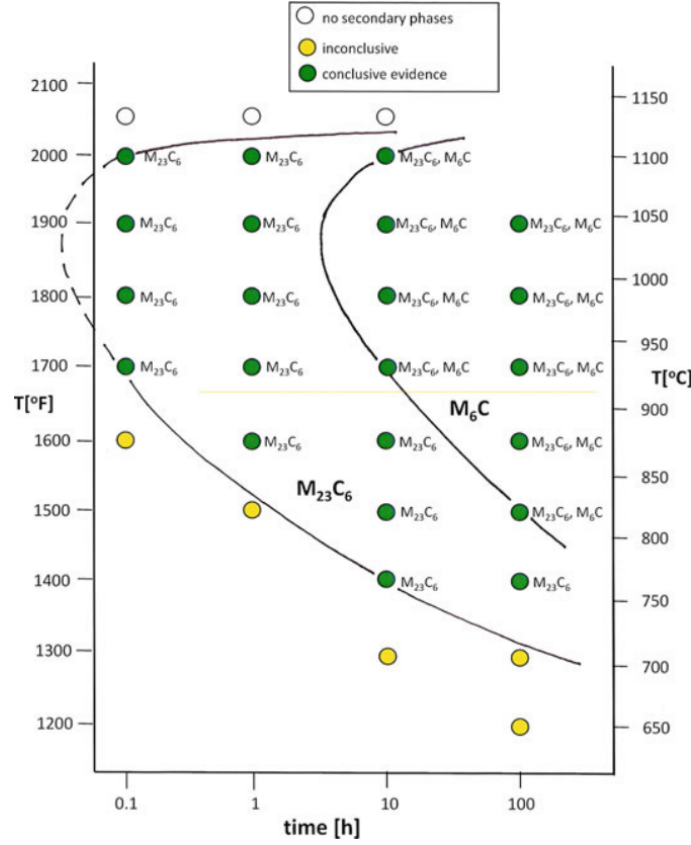


Figure 2.4: TTT diagram of Haynes 282 alloy with proposed C-curves for secondary carbides [12].

Zhang et al. studied the evolution of carbide precipitation during heat treatment of wire arc additive manufacturing (WAAM) obtained Haynes 282. As it is shown in Figure 2.5, the as-built microstructure showed equiaxed sub-micron primary carbides, that were unaffected by the solution treatment of 2 h at 1150 °C and the two ageing steps of 2 h at 1010 °C and 8 h at 788 °C. Mo was reported to migrate out of MC carbides during the second ageing step to form secondary M_6C carbides. $M_{23}C_6$ carbides were only observed after the first ageing step, both along grain boundaries with elongated morphology and equiaxed within the grains. One more time, Mo was found to escape $M_{23}C_6$ to form M_6C during the second ageing step [16].

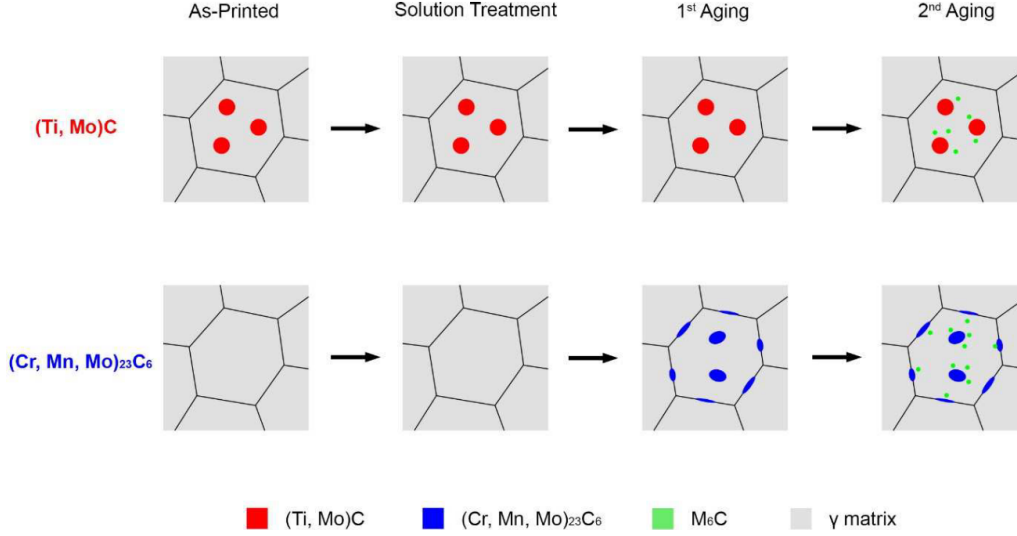


Figure 2.5: Carbide evolution schema for WAAM produced Haynes 282 [16].

Extensive work exists on the effects of long term thermal exposure (LTTE) on this alloy. Damodhar Naidu et al. studied the effects of up to 2000 h exposure at 760 °C on Haynes 282 plates. They reported a microstructural evolution characterized by an increase in matrix grain size and γ' precipitates, together with a growth in size and density of secondary carbides along the grain boundaries [17]. They also reported a shift in XRD peaks towards lower 2θ angles with increased exposure time. Lastly, they found a maximum hardness after 250 h exposure, correlated to a higher volume fraction of γ' precipitates, consequence of the decomposition of primary carbides into secondary carbides and γ' . For longer exposure, they stated that only coarsening of the existing precipitates takes place, resulting in hardness decrease.

On a similar manner, Yang et al. reported an increase in hardness after up to 1000 h of exposure at 788 °C [14]. The difference in the time required to achieve peak hardness could be attributed to the larger dimensions of the cast samples, which need more time to reach an equivalent microstructural evolution. After 3000 h exposure they reported a more significant γ' coarsening, from 42 to 230 nm, which was correlated to a step decrease in the material's hardness. In contrast to the results from Zhang et al., they observed M_6C precipitation during the first ageing and $M_{23}C_6$ during the second step of the treatment [14].

A longer study was carried out by Li et al. who followed the evolution of the microstructure and mechanical properties during LTTE up to 40000 within the range between 700 °C and 800 °C in cast Haynes 282. From a microstructural point of view, γ' remained spherical and grew according to Ostwald ripening theory at 700 °C and 750 °C. At 800 °C they observed an acceleration in the growth rate (see Fig. 2.6 (a)) and a morphological transition from spherical to cuboidal shape, associated with a transition from an interfacial energy-controlled to a strain energy-controlled process [18]. They also reported precipitation of μ phase, initially around intragranular primary carbides after 3000 h exposure, and

along the grain boundaries after 10000 h at 750 °C. It showed a needle-like morphology and a semi-coherent interface with the matrix, which explains the earlier intragranular precipitation. Moreover, early Mo depletion due to preferential carbide precipitation in the grain boundaries might have suppressed the precipitation of μ . The volume fraction of μ was found to increase with exposure time [18].

μ phase is characterized by its rhombohedral unit cell and a theoretical stoichiometric composition A_6B_7 . However, in practice, it can present a wide range of stoichiometry [19]. TCP phases precipitate from the γ phase, so γ' forming elements such as Ti and Al contribute to TCP formation by concentrating the γ partitioning TCP forming elements, such as Cr and Mo, in the matrix [19]. TCP phases form preferentially in the vicinity of MC carbides, where refractory elements are rejected into γ . The effects of carbides in TCP phases formation is not completely clear. There can be competition for solutes, where a higher carbide presence leads to a reduction in TCP phases, or preferential precipitation in carbide's vicinity due to structural relationships, as it has been reported for example between M_6C and μ [19].

It is generally accepted that the TCP phases have a negative effect in the mechanical properties of the alloys. In part due to their brittle nature leading to the formation of cracks, but also because of the softening of the matrix due to solute depletion, which in turn reduces solid solution strengthening [19]. Nonetheless, some studies suggest that the TCP volume fraction can be too low to have a significant effect on the mechanical properties [20], [21].

Regarding mechanical properties, Li et al. also performed tensile testing at 750 °C to samples exposed to the same temperature. As shown in figure 2.6 (b), they observed an initial strengthening up to 3000 h followed by a deterioration, linked to a transition in dislocation movement mechanisms. Regarding ductility, a minimum was reached for 1000 h, associated to grain boundary weakening due to carbide coarsening. After 10000 h exposure, the lower strength found was related to pronounced γ' coarsening and the higher ductility to μ acting as crack source, increasing dimple density in the fracture process [18].

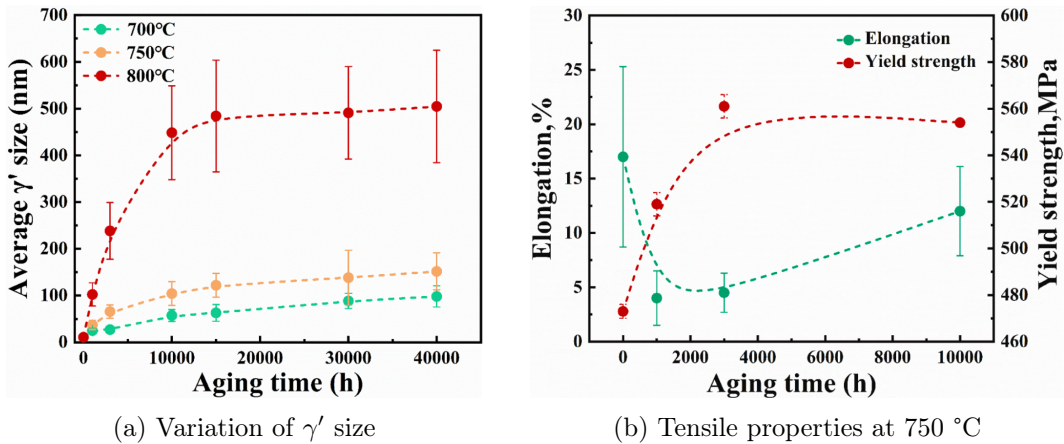


Figure 2.6: Overview of LTTE experimental results [18].

A similar to μ needle-like phase was reported by Magnin et al. after exposing PBF processed Haynes 282 for 1000 h at 750 °C in CO_2 atmosphere at 20 MPa. Even though it was hypothesized that it could correspond to η phase due to its growth around γ' precipitates, this could not be confirmed [22]. The presence of this phase was reported for a similar alloy, Haynes 263, after LTTE. Nonetheless, its precipitation was delayed and reduced by increasing the Al content, which is already higher in Haynes 282 [23].

Regarding the effect of the atmosphere in the LTTE evolution of the alloy, both Magnin et al. and Brittan et al., who also tested Haynes 282 in CO_2 and Argon at 750 °C for 1000 h, reported that reduction of mechanical properties is due to the effects of thermal ageing rather than corrosion [22], [24].

Pike also studied the effects of LTTE on Haynes 282, specifically up to 1000 h exposure of 1.6 mm sheets subjected to standard ageing treatment beforehand. He performed extensive characterization of the tensile properties both at room temperature (RT) and at exposure temperatures of 649, 760, 816 and 871 °C. After 1000 h exposure, the highest drop in elongation (nearly 50 %) was observed at 816 °C. Room temperature yield strength increased after exposure at 649 °C and 760 °C but decreased for higher temperatures. Regarding the microstructure, as it is shown in Figure 2.7, 649 °C exposure did not produce noticeable differences, and higher temperatures resulted in γ' coarsening. At 816 °C a transition to cuboidal morphology was also noticed. The observed phases were identified as primary TiN and MC, and secondary $M_{23}C_6$ and M_6C . No TCP phases were observed in any condition [25].

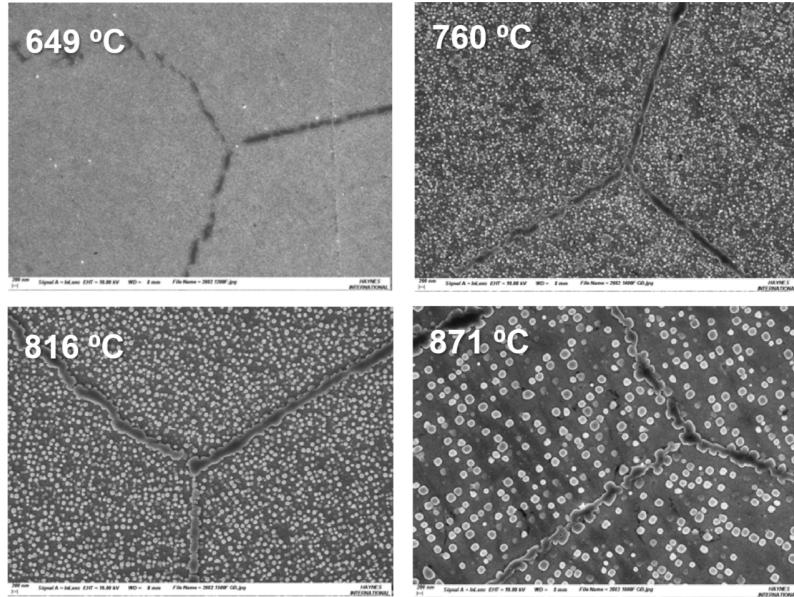


Figure 2.7: Haynes 282 microstructure after 1000 h exposure at different temperatures [25].

He also performed longer exposures on 12.7 mm plates, up to 16000 h, starting from the standard aged condition. Regarding RT properties, elongation drop was consistent with the previous results, with a maximum of 50% decrease at 760 °C after 4000 h. Longer

exposure did not modify it further. For 871 °C exposure, the elongation was found to be independent of the exposure time. Tensile yield strength increased about 15% after 100 h exposure at 649 °C and remained constant after that. At 760 °C it initially increased and then decreased gradually, retaining 93 % of the initial strength after 16000 h. Finally, 871 °C exposure resulted in a more pronounced decay, that slowed down after 4000 h and resulted in a 34 % reduction [25].

Lastly, testing at exposure temperature resulted in an elongation decrease and strength increase at 649 °C, and the opposite for higher temperatures. At 760 °C the alloy retained 86 % of its initial strength, and at 871 °C, 49% [25].

A summary of the main reported results on Haynes 282 LTTE is shown in tables 2.3 and 2.4.

Table 2.3: Summary of existing research on LTTE effects on Haynes 282.

Sample Type	Temp. (°C)	Time (h)	Grain Size (μm)		γ' Size (nm)		Hardness (HV)		Source
			Initial	Final	Initial	Final	Initial	Final	
Plate	760	50	42	43			334		[17]
Plate	760	100	42	44			334		[17]
Plate	760	250	42	48	29	38	334	372	[17]
Plate	760	500	42	50			334	360	[17]
Plate	760	1000	42	55	29	58	334	359	[17]
Plate	760	2000	42	56	29	70	334	359	[17]
Plate	760	4000			20	100			[26]
Cast	788	100			-	42	250	281	[14]
Cast	788	1000			-	102	250	315	[14]
Cast	788	2000			-	119	250	314	[14]
Cast	788	3000			-	231	250	264	[14]
Cast	700	40000			-	100			[18]
Cast	750	40000			-	152			[18]
Cast	800	40000			-	500			[18]
Cast	800	3000			-	238			[18]
PBF-LB	850	1000			83	150-200			[27]

Table 2.4: Summary of existing research on LTTE effects on Haynes 282.

Sample Type	Temp. (°C)	Time (h)	TYS (MPa)		UTS (MPa)		Elongation (%)		Source
			Initial	Final	Initial	Final	Initial	Final	
Plate	760	4000	715	707	1147	1205	–	–	[26]
Sheet	649	1000	693	778	1128	1191	31	26	[25]
Sheet	760	1000	693	718	1128	1176	31	23	[25]
Sheet	816	1000	693	634	1128	1102	31	21	[25]
Sheet	871	1000	693	502	1128	975	31	24	[25]
Sheet	649	1000	608	680	991	1037	27	24	[25]
Sheet	760	1000	598	639	823	818	22	27	[25]
Sheet	816	1000	551	426	677	581	19	37	[25]
Sheet	871	1000	494	260	552	405	23	44	[25]

2.2 Additive manufacturing (AM)

Additive manufacturing (AM) technologies, also known as 3D printing, originated as rapid prototyping techniques initially meant to fabricate test units before mass production [28]. However, the field has largely evolved to become a cutting-edge manufacturing technology specially suitable for the creation of highly complex and personalized components that would be impossible to manufacture using traditional techniques. According to the ISO 52900 standard, 7 groups of techniques can be distinguished: Binder Jetting, Directed Energy Deposition, Material Extrusion, Material Jetting, Powder Bed Fusion, Sheet Lamination and Vat Photopolymerisation [29].

These processes are based on the addition of material layer by layer to create objects from 3D model data. In contrast to traditional subtractive manufacturing, this results in minimal material waste and a high potential for the production of intricate geometries and customized parts [30]. Nonetheless, there are several challenges in AM associated with limitations in materials, part size and mechanical properties [30] that need to be taken into account when developing the manufacturing process.

2.2.1 Powder Bed Fusion - Laser Beam (PBF-LB)

Among the Powder Bed Fusion (PBF) technologies, selective laser melting (SLM), also known as Powder Bed Fusion-Laser Beam (PBF-LB) or Laser-Powder Bed Fusion (L-PBF), is a widespread technique used to produce high quality parts in various industries, ranging from medicine to aerospace [31]. The working principle of this technology, illustrated in Figure 2.8, is the localized fusion of powder due to the thermal energy input from a laser. The laser follows a predefined trajectory, leaving behind a track of melted material. Once a layer is completed, the printing bed is lowered, a new layer of powder is spread on top with a roller, and the cycle repeats until the part is completed [30].

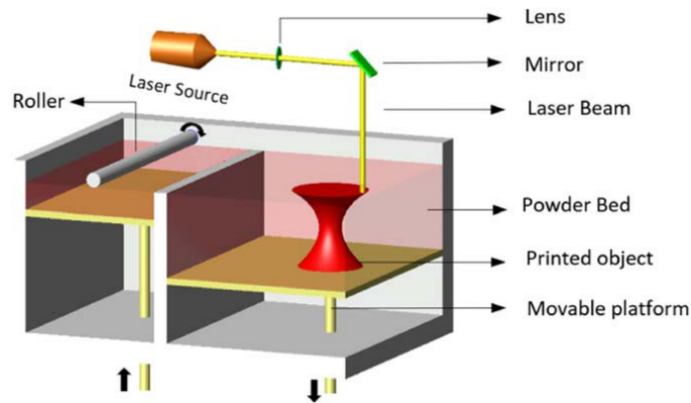


Figure 2.8: PBF-LB process schema [31].

There are several process parameters that need to be optimized in order to produce high quality parts. As shown in Figure 2.9 these include the laser power, hatch spacing, scanning speed and layer thickness [32]. Moreover, they have to be considered together

with powder properties, such as size distribution and morphology, and material properties like absorptivity spectrum, melting temperature range and thermal conductivity. With the correct process design, PBF-LB parts can achieve a near 100% density and strength comparable to their traditionally manufactured counterparts [32]. An intrinsic characteristic of this process is the material exposure to high thermal gradients and cooling rates. This results in anisotropy and residual stresses and may induce different defects such as warping and microcracks [30]. Moreover, due to the large surface area of the powder, even when the process is usually carried out under an inert atmosphere, higher oxygen content has been reported in PBF-LB produced parts [33].

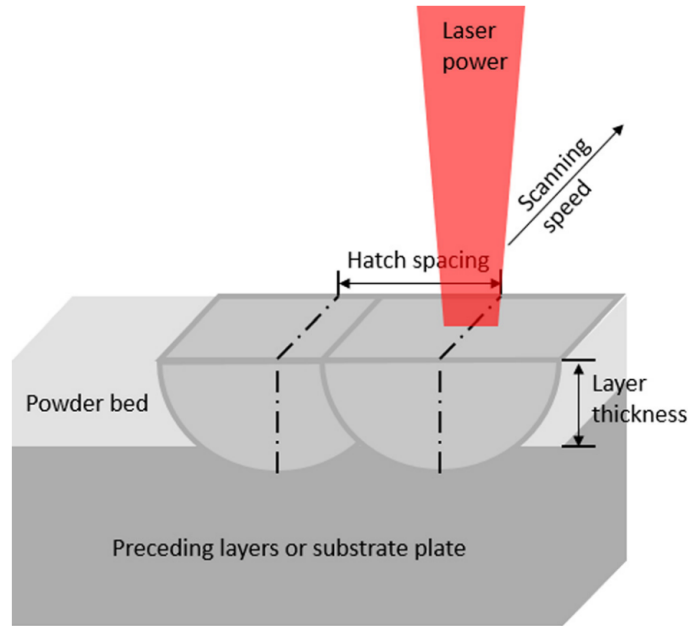


Figure 2.9: PBF-LB process parameters [32].

Defect free PBF-LB of Haynes 282 was initially thought to be feasible due to its chemical composition. The relatively low Al and Ti content helps to slow down γ' precipitation kinetics, that otherwise would result in large shrinkage stress and cracking, analogous to what has been observed during welding in other γ' strengthened superalloys [34].

In this context, PBF-LB processing of Haynes 282 has been researched due to its potential for the fabrication of high added value parts, as it can achieve high strength and thermal stability despite its relatively low γ' content [13]. Hariharan et al. presented an integrated computational materials engineering (ICME) approach to predict segregation during PBF-LB solidification in Haynes 282 and used this data as input to simulate homogenization and microstructural evolution during post-processing heat treatments. They concluded that due to the small scale of segregation in PBF-LB, a homogenization step after printing is not necessary, as nominal composition is reached within 10 minutes at 1010 °C (standard first ageing step temperature). They validated the model results by comparing predicted and experimental γ' size, and reported an agreement between the results [15].

Otto et al. studied the influence of printing parameters and identified microcracks associated with grain boundary precipitates during initial tests. Nonetheless, they managed to define a process window to produce crack-free PBF-LB Haynes 282 samples [35].

Following this path, Shaikh et al. successfully manufactured crack-free samples with full density. Mechanical testing of heat treated specimens revealed a higher room temperature yield strength compared to wrought reference material that was attributed to grain size hardening. Moreover, strength was higher in the horizontal direction, where grain size perpendicular to the stress application was smaller. When tested at 800 °C, strength was similar to that of the plate, potentially due to the reduced effect of grain size strengthening at high temperature. Ductility at high temperature was found to be lower than the reference, and fracture analysis linked this to grain boundary carbides acting as fracture initiation sites [36].

Regarding the microstructure, they observed a dendritic solidification microstructure along the building direction in the as-built condition and visible melt tracks stacked in layers. After standard heat treatment (SHT), the melt tracks were no longer visible, and carbide precipitation was observed in the grain boundaries. Carbide morphology was the main difference with the wrought reference, as blocky MC primary carbides were not observed. Instead, all the carbides were smaller and discontinuous in the grain boundaries. The microstructure after treatment remained anisotropic, with long elongated grains in the building direction and small equiaxed grains in the perpendicular plane [36].

Christofidou et al. investigated the effect of post-processing thermal treatments and long term thermal exposure in PBF-LB produced Haynes 282 samples. Partial recrystallization of the as-built samples was observed after 1 h exposition at 1190 °C with complete recrystallization in the same time frame at 1250 °C. This temperature is much higher than the γ' solvus temperature, usually linked to recrystallization. A proposed explanation for this phenomenon is an increased activation energy due to the carbide distribution in the cellular colonies. Even after recrystallization, they measured a grain aspect ratio of 2, still biased towards the build direction. Moreover, they found extensive recrystallization twins. They did not observe MC carbides in any of the samples. [27].

After 1000 h exposure at 850 °C in inert atmosphere, they observed similar microstructures in every condition, characterized by coarsened γ' and secondary carbides. The non recrystallized samples exhibited a discrete distribution of grain boundary carbides while the recrystallized ones showed a more continuous morphology.

2.3 Hot Isostatic pressing (HIP)

Different post-processing treatments can be applied to PBF-LB produced parts. For instance, grinding, polishing, or shot peening to improve surface finish; or thermal annealing to relieve residual stresses [30]. In this context, Hot Isostatic Pressing (HIP) can be used as a thermomechanical post-processing step to minimize porosity, heal microcracks, relieve stresses and reduce anisotropy through recrystallization [35]. HIP consists on the simulta-

neous application of pressure up to 200 MPa and temperature up to 1450 °C and can be used both as a fabrication technique and as a post-processing step. It is not only employed in AM but also in powder metallurgy, casting and metal injection moulding [37].

Antecedents of applying HIP post-processing to PBF-LB processed Haynes 282 include the work of Otto et al., who reported complete recrystallization, extensive twinning, micro-cracks healing and densification after a HIP cycle of 6 hours at 150 MPa and 1050 °C in as-built samples [35]. Deshpande et al. also observed recrystallization from as-built samples after a shorter cycle at higher temperature, lasting 3.5 hours at 1185 °C and 150 MPa [38]. In contrast to Christofidou et al., they reported equiaxed grains, that eliminated the anisotropy of mechanical properties. After this cycle, they also reported dissolution of a dendritic phase present in the as-built condition as well as fine γ' (average diameter of 10 nm) and grain boundary carbides precipitation. Lastly, regarding mechanical properties, the HIPed samples showed strength, elongation and hardness comparable to that of the as printed condition, and lower than the traditionally heat treated counterparts. This was attributed to grain growth during the HIP process, that balanced out the hardening effect of the γ' precipitates [38].

On a similar manner, Shaikh et al. focused on the high temperature performance from PBF-LB samples by comparing the microstructure and mechanical properties among different solution heat treatments: 1135 °C and 1250 °C for two hours, and a HIP cycle of 4 hours at 1250 °C and 100 MPa (all followed by the standard two-step ageing procedure). They reported a reduction in count, area fraction, density and maximum size of defects in the HIPed sample compared to the other conditions. A higher fraction of coarser grains in the build direction after HIP compared to the other specimen solubilized at 1250 °C was also noted. Both conditions exhibited significant grain growth, weaker texture and extensive twinning compared to the 1135 °C sample. Carbide distribution was found to be interconnected after 1250 °C processing but discontinuous after the 1135 °C treatment. In all cases, carbides were sub-micron-sized and also present intragranularly. This was attributed to grain growth at higher temperatures resulting in reduced grain boundary area for carbide precipitation. It remained unclear whether grain growth was preceded by static recrystallization or not, due to the non-equiaxed morphology of the grains [39].

Regarding mechanical properties, they reported a higher yield strength but also a higher anisotropy for the lower temperature sample, both at room temperature and at 760 °C. Nonetheless, this sample also showed a significantly lower ductility at high temperature in the horizontal direction. At the same time, the HIPed sample showed a higher elongation at high temperature than its counterparts. This was attributed to defect healing during the HIP cycle retarding the coalescence of voids. In contrast to tensile testing results, high temperature low stress creep behaviour was superior in the high temperature treated samples. This was attributed to the bigger grain size reducing diffusional flow at grain boundaries. PBF-LB samples showed longer life than the wrought reference material, which could have been related to the more tortuous grain boundaries geometrically inhibiting sliding [39].

Even though extensive characterization of Haynes 282 is available, there is a lack of published literature regarding the use of HIP as a combined post deposition treatment, aiming to integrate the solution and ageing process. This strategy could reduce processing time and energy consumption, while also taking advantage of the defect-healing capabilities of HIP. As a result, it could potentially allow saving costs and simultaneously improve the quality of the final product. While preliminary strategies for such treatments were proposed by Perez de Arriluzea et al. [40], their long-term stability remains unexplored. Understanding the effect of long-term thermal exposure on HIPed PBF-LB Haynes 282, particularly regarding the microstructural evolution and the consequences on its mechanical properties, is critical for evaluating the reliability of components in high-temperature service. To address this gap, the following chapter details the experimental methodology employed in this study.

2.4 Material characterization techniques

2.4.1 X-ray diffraction (XRD)

X-ray diffraction (XRD) is a characterization technique based on the diffraction produced as the result of the interaction between waves and periodic structures [41]. The equipment, shown in Figure 2.10, produces monochromatic X-ray radiation, which has a wavelength of similar magnitude to crystal lattices. The beam shines into the sample and intensity peaks from its reflection are produced at specific angles, where the Bragg equation (Eq. 2.3) is fulfilled. The XRD diffractograms are considered the fingerprint of the atomic distribution within the sample, since the atomic positions, interplanar spacings, and relative intensities are specific to each crystal.

$$n\lambda = 2d\sin\theta \quad (2.3)$$

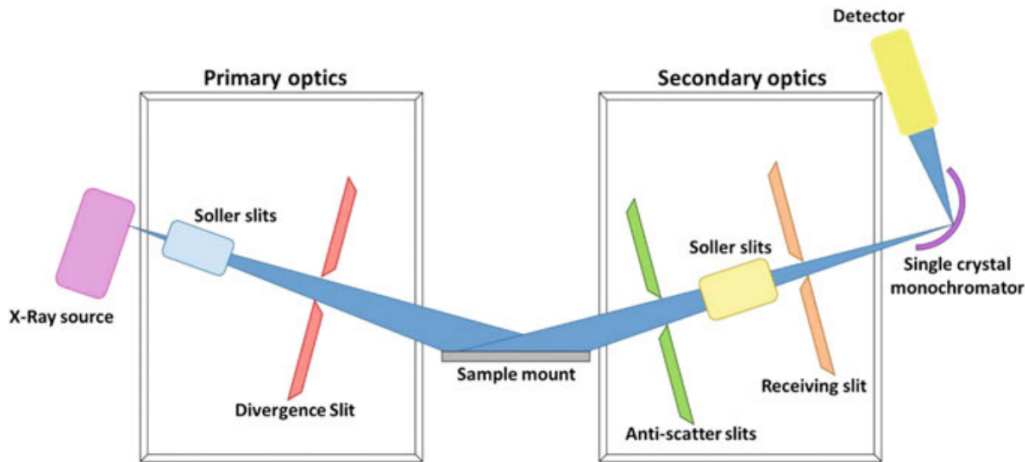


Figure 2.10: XRD schema [41].

There are different variables that affect the XRD diffractogram from a material, including residual stresses, temperature, surface finish and domain size. The domain size effect is governed by the Scherrer equation (Eq. 2.4), where λ is the wavelength of the incident X-ray radiation, β the peak full width at half maximum (FWHM) in radians, L_{hkl} the domain size perpendicular to the hkl plane and θ the diffraction angle. This effect is noticeable in the 25–100 nm crystallite size range, as bigger sizes lead to little broadening, and the peak width is governed by the instrument resolution; while for smaller sizes the excessive broadening leads to a drop in intensity and peak overlapping hinders their analysis [42].

$$L_{hkl} = \frac{\lambda}{\beta \cos \theta} \quad (2.4)$$

XRD is often used to characterize the structure of Ni-based superalloys. Besides its capability to identify the presence of different phases, one notable application is the determination of the lattice misfit between the precipitates and the matrix, which is known for having a remarkable effect on the microstructure of the alloy. This can be calculated from the peak positions according to Eq 2.3. However, due to the small difference in the lattice parameter, the reflections are often not clearly resolved and might even be completely overlapped [43]. Other factors that make the peak indexing more difficult include the strain fields around the precipitates and peak broadening due to the size effect [43]. For these reasons, sample preparation, scanning and post-processing strategy needs to be carefully optimized.

Adequate surface preparation is needed not only to ensure a flat surface but also because the penetration depth in XRD is in the order of tens of micrometers, and follows the exponential radiation attenuation law [44]. This means that the surface condition, including roughness, defect density and residuals stresses can modify the diffractogram, in particular, the FWHM of the peaks [44].

Regarding the scan, systematic errors associated to equipment misalignment, sample displacement and flat specimen error need to be taken into account [45]. Other errors include the non strictly monochromatic nature of the incident radiation and the diverging nature of the beam [46]. Lastly, regarding the scan parameters, a longer dwell time helps to improve the signal-to-noise ratio, and a small step size leads to a higher angular resolution.

From a practical point of view, instrumental error can be contemplated performing a scan of a standard sample of known crystalline structure and crystallite size. Silicon powder is typically used [47] for this purpose. Given that the phases in a sample are known, Rietveld refinement method [48] can be employed for quantitative analysis of the diffractogram, contemplating instrumental error. This method uses a pattern fitting approach to calculate a diffractogram, which is then compared to the experimental one and refined by least-squares. By doing this, weight fraction of phases and crystallite size can be calculated [49].

Even with these considerations, in some cases it is not possible to resolve the lattice misfit using XRD of the bulk material. An alternative to overcome this problem is to extract the precipitates by electrochemical dissolution of the matrix to measure them in a different scan. However, by doing this the elastic strain between the phases is eliminated, and the measured lattice parameters correspond to the so-called unconstrained condition [43].

Even though γ and γ' crystalline structures are closely related, they are part of different space groups: Fm-3m and Pm-3m, respectively. For this reason, some reflections are forbidden for γ but not for γ' . These are called superlattice reflections and can help to identify the presence of γ' , that would otherwise be difficult or impossible to distinguish from the γ peaks due to their closeness in lattice parameters [50].

Chapter 3

Experimental procedure

3.1 Materials and processing

3.1.1 Printing

The characterization of the Haynes 282 gas-atomized powder, provided by Powder Alloy Corp., was previously carried out by Perez de Arriluzea et al. [40]. Particle size distribution was measured using a Sympatec QICPIC dynamic image analysis system, resulting in a volume mean diameter of 34 μm . Chemical composition was characterized via a Varian 725-ES inductively coupled plasma optical emission spectroscopy (ICP-OES) spectrometer. A LECO CS-200 series carbon/sulphur combustion analyser and a LECO ONH 836 series oxygen/nitrogen/hydrogen inert gas fusion analyser were used to determine the content of interstitial elements. These results, which serve as the baseline for the current study, are shown in Table 3.1. Traces of W, Nb, Ta and Cu were also detected in the powder, all within their admissible range, below 0.1 Wt.%.

Table 3.1: Nominal and powder Haynes 282 chemical composition. Adapted from [40].

Element	Nominal (Wt. %)	Powder (Wt. %)
Nickel	Balance	Balance
Chromium	20	19.9
Cobalt	10	10.4
Molybdenum	8.5	8.85
Titanium	2.1	2.16
Aluminium	1.5	1.49
Iron	1.5 max.	0.12
Manganese	0.3 max.	0.02
Silicon	0.15 max.	0.03
Carbon	0.06	0.05
Boron	0.005	0.006
Oxygen	-	0.01
Nitrogen	-	0.02

The printing process was carried out by Aenium Additive systems, using an EOS M290 PBF machine. The process parameters, shown in Figure 3.2 were optimized to minimize

defects such as micro-cracks and voids. 11x11x11 mm cubes for metallographic examination as well as 80 mm long and 11 mm diameter bars for tensile testing were produced. As AM products are characterized by their anisotropy, the orientation of the samples needs to be tracked. As shown in Figure 3.1, the load axis of the tensile samples was set parallel to the build direction. Cubes for metallographic examination were sectioned in two perpendicular planes: "Z" and "XY" parallel and perpendicular to the build direction respectively.

Table 3.2: PBF-LB printing parameters.

Bed Temp. (°C)	Atmosphere	VED (J/mm ³)	Layer Thickness (μm)
200	Ar	62	50

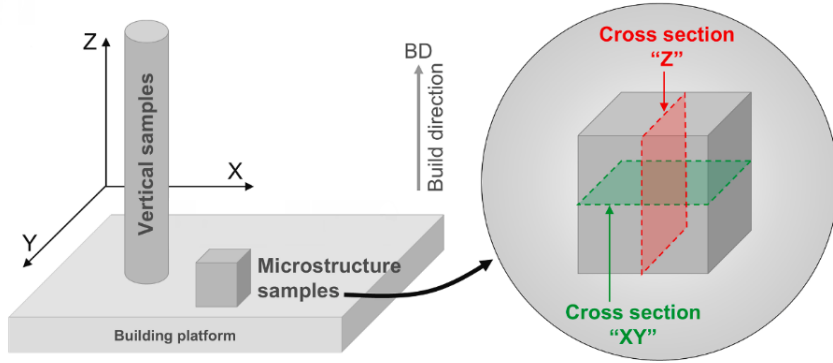


Figure 3.1: Sample orientation schema. Adapted from [36].

3.1.2 Post processing

The different combinations of post-printing treatments are shown in Table 3.3. The heat treatment parameters and strategies employed in this study were adopted from the work established by Perez de Arriluzea et al. [40]. Sample 1 was kept in the as-built condition; samples 2 to 5 were treated in HIP, followed by the standard heat treatment (SHT) steps (Fig. 3.2). Note that due to technical limitations the cooling rate (CR) after the HIP treatment is too low to completely retain the high temperature microstructure. In every case, the samples were cooled down to RT between steps. Sample 6 corresponds to the SHT (Fig. 3.3), which consists on a solutioning step, followed by a two-step ageing. Samples 7 and 8 were solutioned and first-aged in HIP (with a higher cooling rate after the solutioning), and cooled down directly to first ageing temperature. Afterwards, sample 8 was cooled down to RT to perform the second ageing at atmospheric pressure (Fig. 3.4). Finally, sample 9 was subjected to the full CombiHIP treatment (Fig. 3.5), industrially carried out at Hiperbaric with a higher cooling rate after solutioning and only cooling to RT after the second ageing. For every sample the HIP steps were carried out at 150 MPa. All treatments were performed under an inert argon atmosphere.

Table 3.3: Different applied post-printing treatments. Bold characters indicate HIP steps.

Sample	HIP annealing	CR (°C/min)	Solution annealing	CR (°C/min)	First ageing	CR (°C/min)	Second ageing	CR (°C/min)
1								
2	1185°C 2h	50						
3	1185°C 2h	50	1135°C 2h	140				
4	1185°C 2h	50	1135°C 2h	140	1010°C 2h	20		
5	1185°C 2h	50	1135°C 2h	140	1010°C 2h	20	788°C 8h	20
6			1135°C 2h	140	1010°C 2h	20	788°C 8h	20
7			1185°C 2h	110	1010°C 2h	20		
8			1185°C 2h	110	1010°C 2h	20	788°C 8h	20
9			1185°C 2h	140	1010°C 2h	20	788°C 8h	20

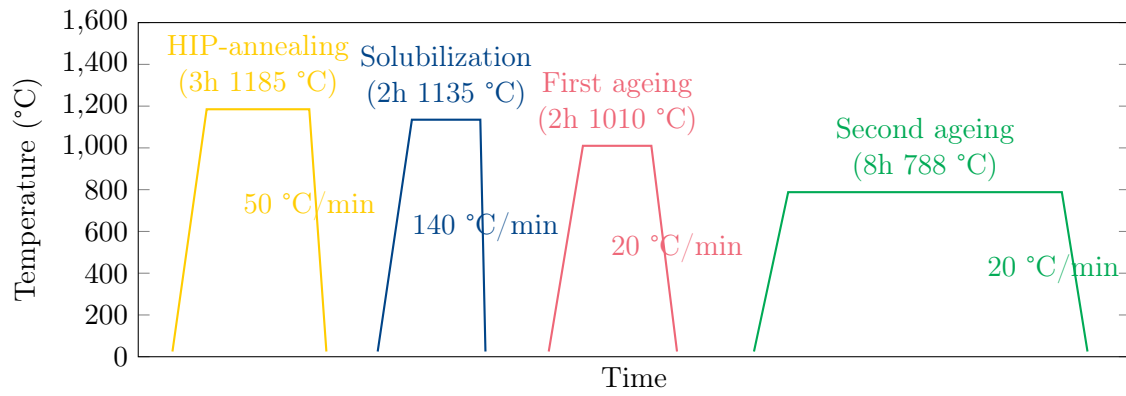


Figure 3.2: HIP annealing + standard heat treatment steps.

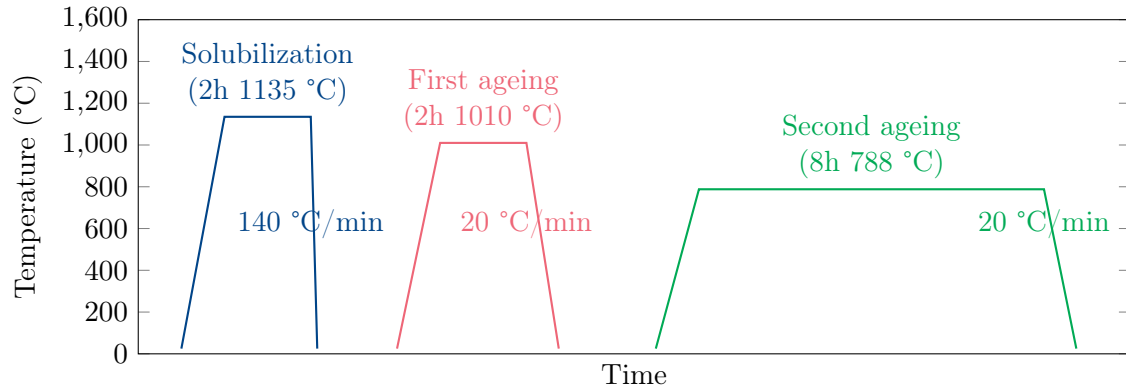


Figure 3.3: Standard heat treatment steps.

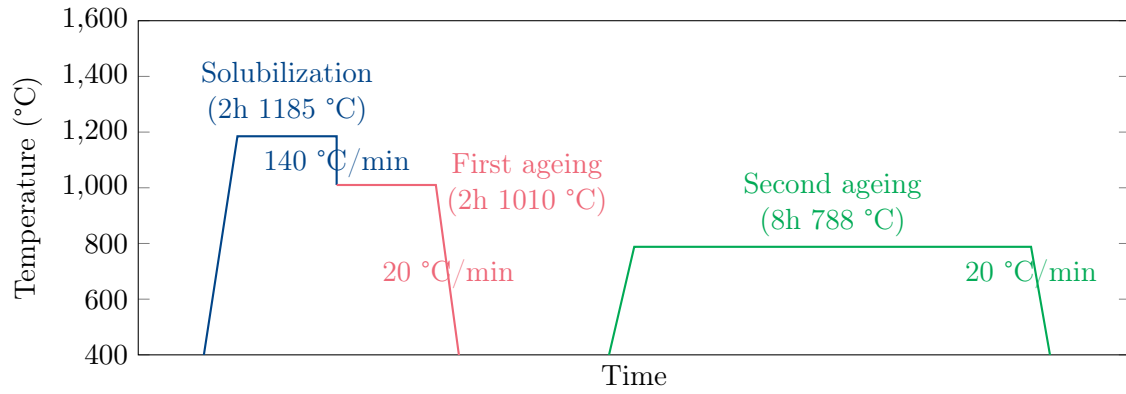


Figure 3.4: Partial CombiHIP heat treatment steps.

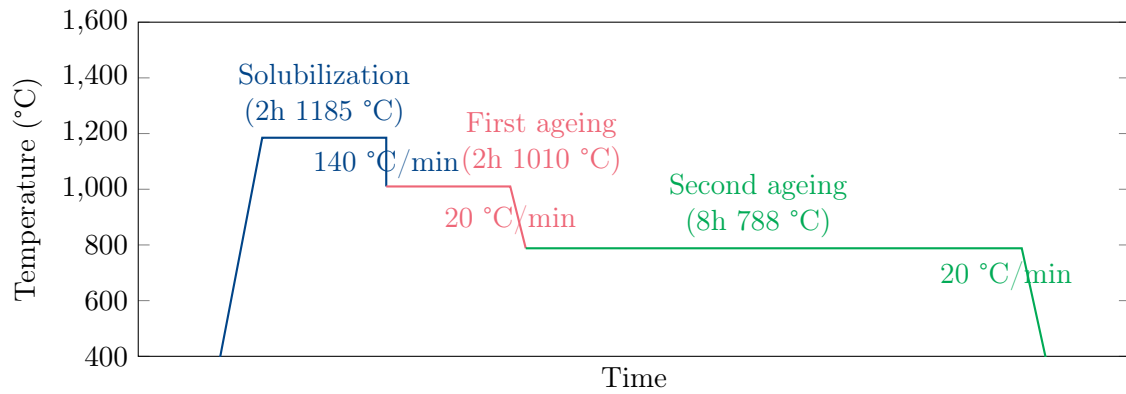


Figure 3.5: CombiHIP heat treatment steps.

3.1.3 Long term thermal exposure (LTTE)

The samples processed through the CombiHIP route were subjected to different long term thermal exposure treatments to simulate working conditions. The selected parameters are shown in Table 3.4. The treatments were performed in a Thermolyne 48000 muffle furnace under a non-controlled atmosphere. A heating ramp of 10 °C/min to the target temperature was applied, followed by a 500 h hold and furnace cooling. Furnace temperature was verified with an external thermocouple throughout the complete cycle.

Samples 10, 11 and 12 correspond to the same printed and HIP post processed specimen, cut parallel to the build direction for posterior microstructural examination. In the 760 °C treatment, three tensile samples were exposed together with sample 10.

Table 3.4: Long term thermal exposure treatments.

Sample	Temperature (°C)	Time (h)
10	760	500
11	850	500
12	930	500

3.2 Testing and characterization

3.2.1 Mechanical testing

The exposed samples were machined to 6 mm diameter probes, compliant with the ASTM E8 standard, and used for high temperature tensile testing at 760 °C. Tests were carried out in an Instron 5982 universal testing machine equipped with a resistor furnace. A 60 °C/min ramp was applied followed by 30 minutes stabilization before the test start. The strain rate was set to 0.0014 s^{-1} . The temperature was controlled with a thermocouple in contact with the sample and an extensometer was used to acquire more precise data during the elastic deformation. The experimental array can be seen in Figure 3.6.



Figure 3.6: High temperature tensile testing experimental array.

Complimentary Vickers 1 hardness measurements were taken with a Qness Q30A+ durometer according to the ASTM E384 standard. Ten randomly distributed measurements were performed for each sample.

3.2.2 Material characterization

Samples were mounted in Struers Condufast acrylic hot mounting thermoplastic resin with iron filler. Preparation for metallographic examination consisted of two stages. First, grinding was performed using SiC papers from grit sizes 120 to 4000. Once a uniform scratching pattern was achieved, the sample was rinsed in water and rotated 90° before moving to the next grit. The second stage, polishing, was done using 3 μm and 1 μm diamond suspensions to achieve a mirror-like surface finish.

X-ray diffraction (XRD) analysis was performed using a Bruker D8 advance, equipped with a Cu source, a 2 mm collimator and in a line focus Bragg-Brentano configuration. The step size was fixed at 0.02° with a dwell time of 10 s per step. The analyses were performed in the range between 30° and 90° . Complimentary analysis were performed

using a 20 s dwell in the 34°–44° range to improve minor phases detection in the LTTE exposed specimens.

An internal Si pattern was used to calibrate the results, applying a silicon powder-ethanol suspension after the scan, and re-running the analysis with a shorter dwell time and range. The correction process is shown in figure 3.7. First, the experimental pattern with Si was shifted to match the expected position of the silicon peak. Afterwards, the matrix peak of both experimental curves (with and without Si) were aligned by shifting the full experimental diffractogram (without silicon). It is important to notice that in every case the corrections were smaller than the step size fixed for the analysis, which indicates that there was no significant misalignment.

After correction, the peaks were indexed using the Bruker EVA software with the International Centre for Diffraction Data (ICDD) Powder Diffraction File database (PDF-2-2025).

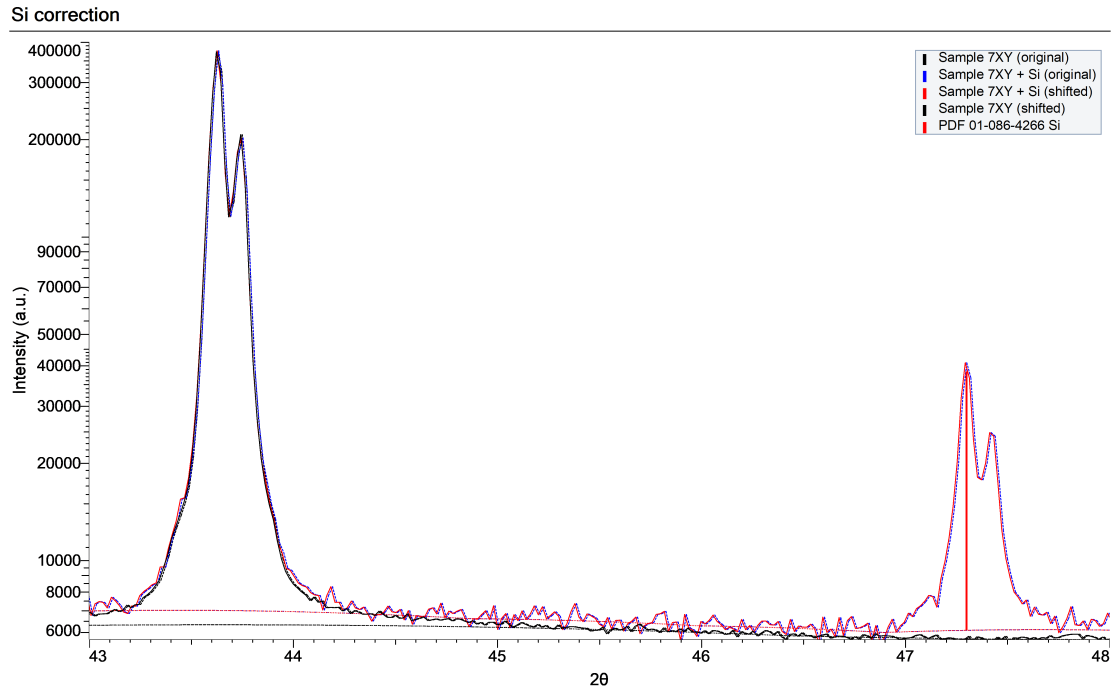


Figure 3.7: XRD diffractograms used for peak positions correction.

The samples were electro-etched in nitric acid applying a 5 V voltage and a 3 A current for approximately 5 s to reveal the microstructure for observation in optical and electron microscopes.

Optical microscopy images were taken with a Leica DMI8 inverted microscope at 50x, 100x, 200, 500x and 1000x magnifications. Within this range it is possible to observe laser tracks, grain structure, grain boundary precipitates and to check for possible defects such as pores or lack of fusion.

To further characterize the microstructure at smaller scale, secondary electrons images were taken with a Zeiss Sigma 500 electron microscope, at an acceleration voltage of 15 kV

and working distance (WD) of 8.5 mm. Electron microscopy makes it possible to capture the topography of the samples in high resolution, allowing the analysis of carbides and precipitates distribution, size and morphology. Moreover, backscattered electron (BSE) images were taken to analyse the element distribution within the constituents of the sample. For better analysis of the precipitates, high magnification images were taken using an InLens secondary electron detector at 5 mm WD and 5 kV accelerating voltage. This detector provides better signal-to-noise ratio and surface detail at lower working distance and accelerating voltage.

In addition to this, Energy Dispersive X-ray spectroscopy (EDS) maps were produced in specific points of interest, as this technique allows the determination of the elements responsible for the variations observed in the BSE images [51]. The accelerating voltage of 15 kV provides an overvoltage ratio greater than 2 for all elements of interest. This ensures the adequate excitation and detection of their characteristic X-rays [51].

3.2.3 γ' precipitates size measurement

As mentioned before, the size, content, morphology and distribution of γ' precipitates plays a major role in the mechanical properties of the alloy. For this reason, a pipeline for particle size distribution measurement was implemented using ImageJ software. High magnification ($150,000\times$) images taken with the InLens detector were used as primary source. Otsu [52] local threshold [53] was applied to produce binary images, with a radius selected based on the sample characteristics (between 20 and 30 pixels). The resulting binary images were subjected to an opening operation, that reduces the noise by first eroding and then dilating the features. The images were then segmented using the watershed algorithm [54] to separate adjacent particles. Finally, the particles were analysed using a minimum size filter that was adjusted to the sample characteristics and a circularity threshold that was fixed to 0.7. By comparing the results from different images, it was observed that this combination of steps provided robust results for the characterization of γ' . A summary of the workflow can be seen in figure 3.8. Due to the high circularity of the particles, Feret diameter was used to estimate the size.

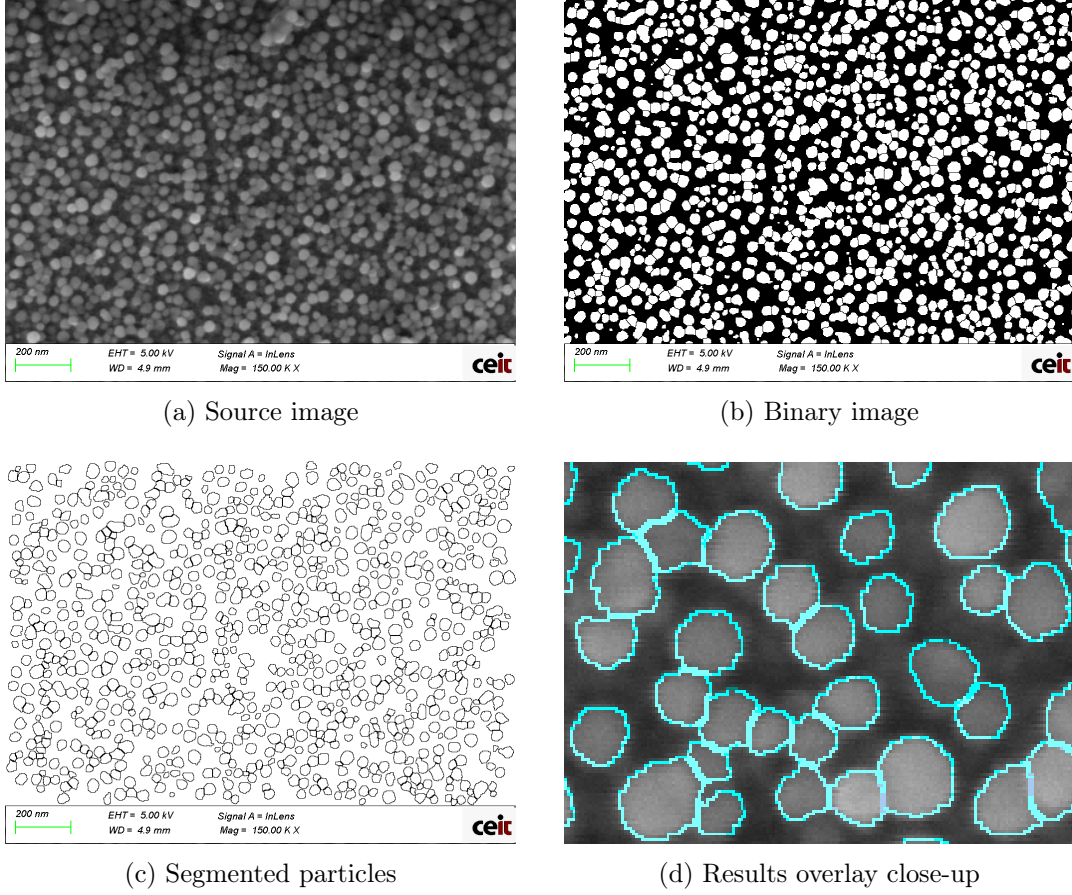
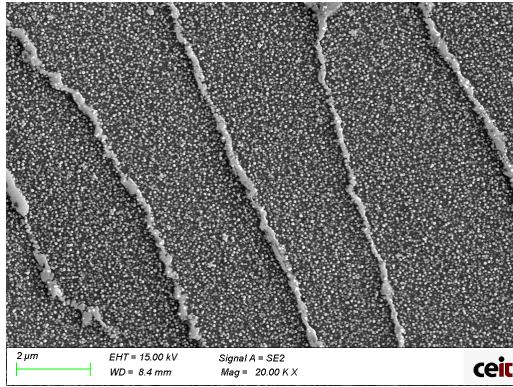


Figure 3.8: Image J workflow for γ' size characterization.

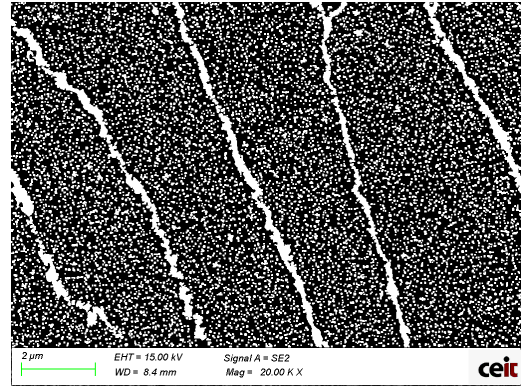
3.2.4 Quantitative carbide characterization

On a similar manner, a carbide analysis pipeline was implemented in ImageJ. Secondary electron images were used as a source, with different magnifications ranging from 10kx to 40kx depending on the size of the features in every sample. Otsu [52] local threshold [53] was applied to produce a binary image, with a radius selected based on the sample characteristics (between 15 and 30 pixels). The resulting binary image was subjected to opening and fill-holes operations.

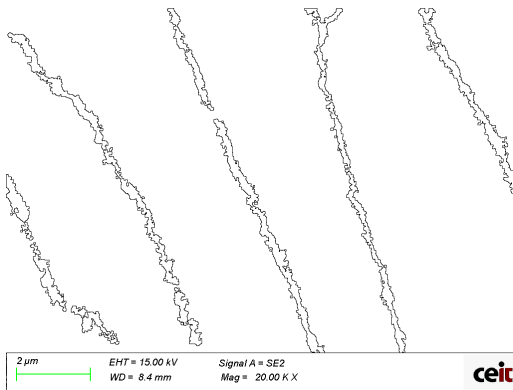
Due to the irregular shape of grain boundary carbides, Feret diameter does not accurately represent true particle size. Instead, an ellipse was fitted to every segmented object and its minor axis was used to measure the thickness of the grain boundary carbide layer. This approach improves the accuracy, particularly for high aspect ratio particles. On the other hand, for discrete intragranular carbides, equivalent circle diameter was used to quantify the results. Finally, the particles were filtered with a minimum size threshold that was adjusted to the sample characteristics. A summary of the workflow can be seen in Figure 3.9.



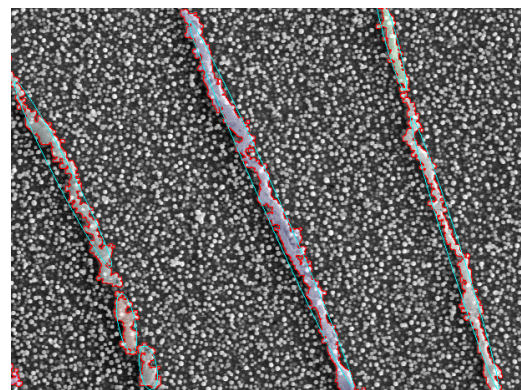
(a) Source image



(b) Binary image



(c) Segmented particles



(d) Results overlay close-up

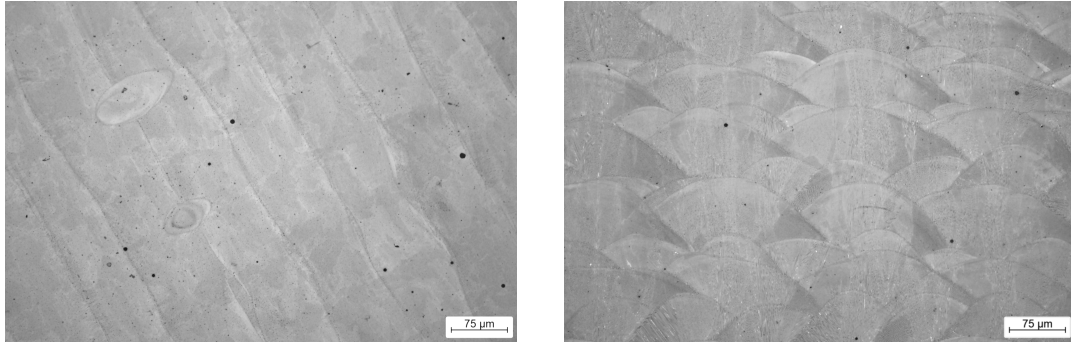
Figure 3.9: Image J workflow for grain boundary carbides characterization.

Chapter 4

Results and discussion

4.1 Post deposition treatments

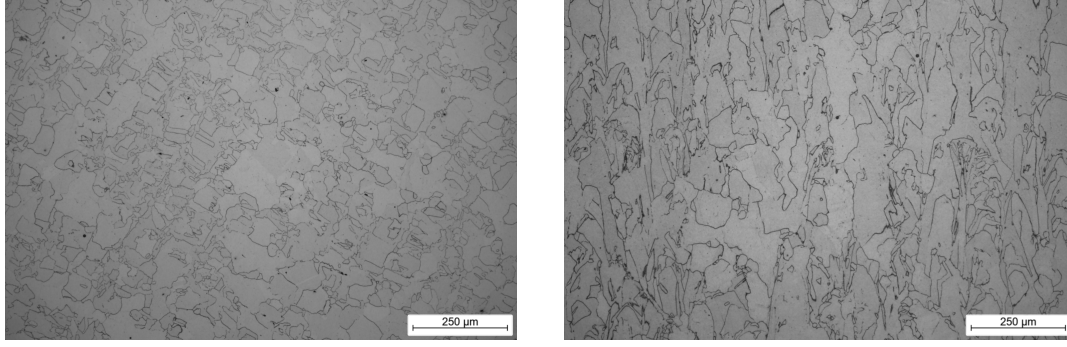
The as-built microstructure can be seen in Figure 4.1. Figure 4.1 (a) shows the XY plane, perpendicular to the build direction, and Figure 4.1 (b) the Z plane, parallel to the build direction. The characteristic PBF-LB laser tracks are visible in both planes. In the Z direction, this is due to the overlapping between the different melt pools from every layer; and in the XY direction, they show the lateral trajectory from the laser. After full heat treatment, and regardless of the processing route applied, the laser tracks are no longer visible due to compositional homogenization (see Fig. 4.2), even though the crystallographic texture is preserved. Grains are coarser and elongated in the build direction, and finer and more equiaxed in the XY cross-section. This is the result of the temperature gradients during the printing process and the root of the anisotropic behaviour of PBF-LB processed materials in the as-built state.



(a) XY plane.

(b) Z plane.

Figure 4.1: As-Built microstructure.



(a) XY plane.

(b) Z plane.

Figure 4.2: Fully heat treated microstructure.

Figure 4.3 shows the microstructure of sample 3, after HIP-annealing (2 hours at 1185 °C and 150 MPa). Grain boundaries do not show a strong contrast due to scarce grain boundary carbides precipitation. However, it can be seen that crystallographic texture is preserved which is an indicator that recrystallization did not occur during the treatment. This statement is also backed up by the XRD analysis, where texture was also observed as an over representation of the (200) γ peak compared to the PDF pattern intensity ratio. As shown in Figure 4.4, this was observed both in the as-built and in the HIP-annealed samples.

There is a lack of consensus regarding the necessary conditions for the recrystallization of HIPed PBF-LB Haynes 282. Some authors observed complete recrystallization after a 3 hours cycle at 1185 °C [38]; while others reported inconclusive evidence after 1250 °C treatments during 2 hours [39]. No signs of recrystallization were observed in the present project for any of the samples after performing HIP cycles of 2 h at 1185 °C. A possible reason for this is that grain boundary carbides, present in the as-built condition, increase the activation energy associated to the process [27].

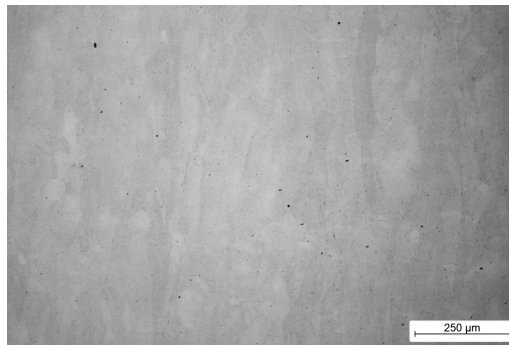


Figure 4.3: HIP-annealed microstructure parallel to the build direction.

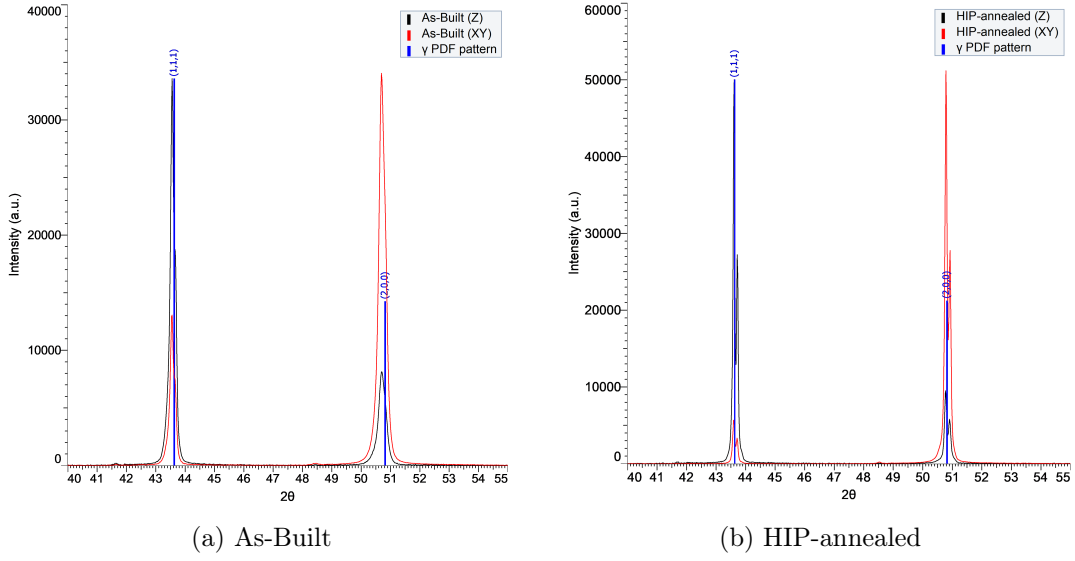


Figure 4.4: XRD diffractograms from as-built and HIP-annealed samples. (200) peak shows a higher intensity in the XY plane.

As shown in Figure 4.5 (a), the HIP-annealed sample exhibits fine γ' precipitates, approximately 20 nm in diameter. It is possible that these originated due to the relatively slow cooling rate after the HIP cycle (50 °C/min). As a result, the material stays 8 minutes in the 600 – 1000 °C range which, according to available studies on γ' precipitation kinetics for this alloy, is enough to nucleate and grow γ' [12], [55], [56]. After the subsequent solutioning step, as shown in Figure 4.5 (b), these γ' precipitates dissolve completely.

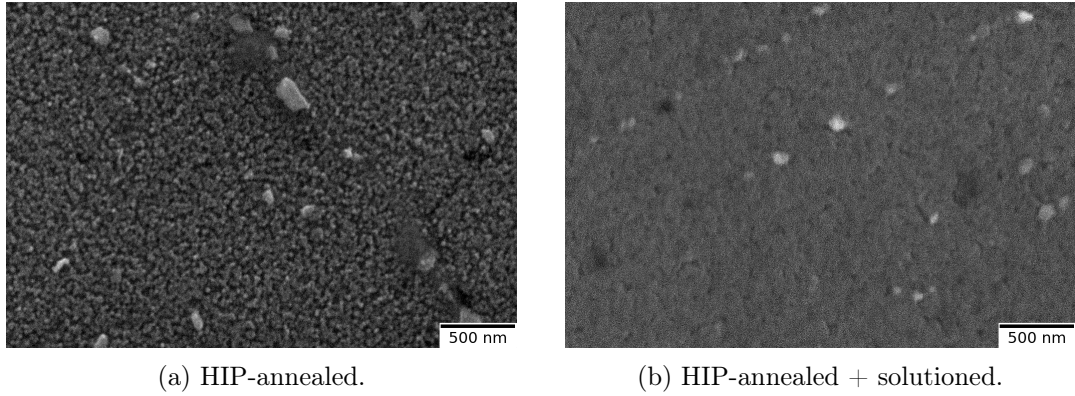


Figure 4.5: γ' precipitates in the HIP-annealed samples.

An overview of the microstructural evolution at different stages of the heat treatment is presented in Figure 4.6. The microstructure after the HIP cycle shows sparse and fine carbides both in grain boundaries and inside the grains. The aforementioned γ' precipitates are not visible at this magnification. After solutioning (S), carbides are not significantly altered but γ' phase is completely dissolved. Figure 4.6 (c) shows that after the first ageing step (A1), there is a substantial amount of γ' precipitates, even though the treatment was carried out at a temperature above the phase solvus. Similar precipitation was observed by Deshpande et al. [38], possibly linked to nucleation and growth during cooling after the

heat treatment. After the second ageing (A2), as shown in Figure 4.6 (d) microstructure seems unaltered and quantitative analysis from the precipitates showed no significant size differences.

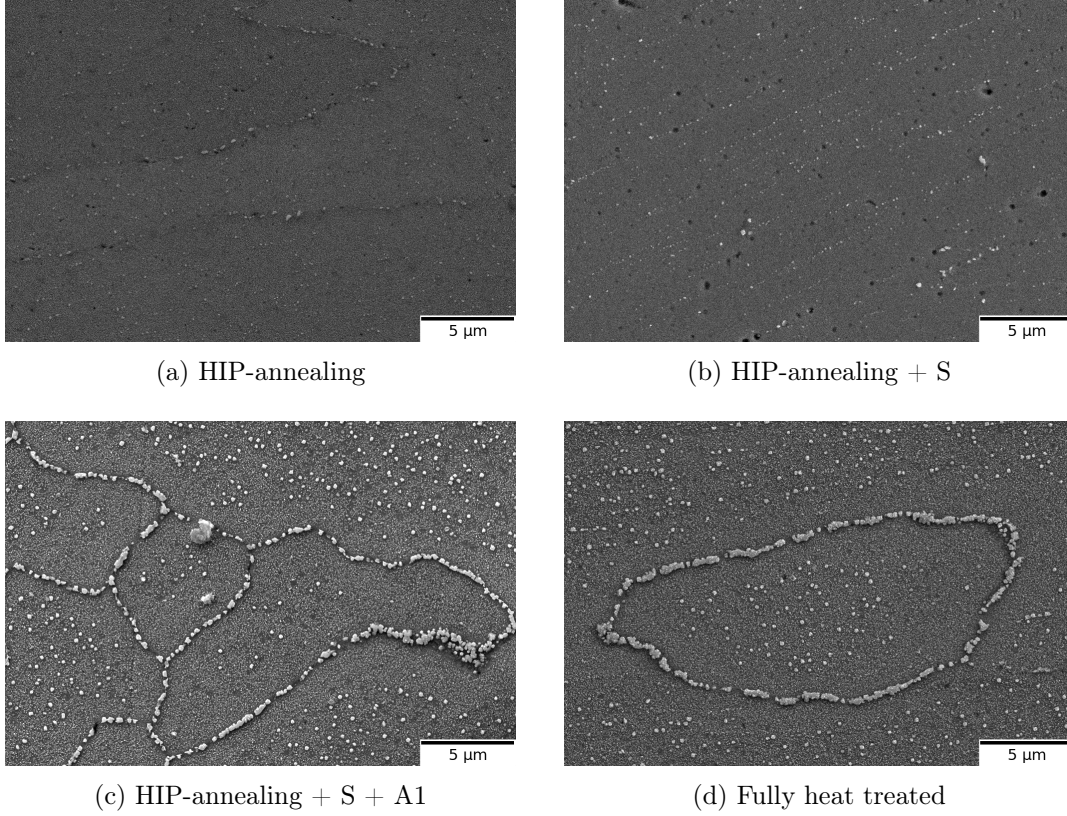


Figure 4.6: Microstructural evolution in the HIP-annealing + SHT route.

Regarding XRD results, stacked visualization from the different samples were created by performing a background subtraction operation, followed by a normalization in the highest peak (γ (111)) and a Y-shift to stack the diffractograms. The peaks were indexed using the Brukers EVA software with PDF-2-2025 database. The selected matching patterns are shown in table 4.1.

Table 4.1: PDF-2 2025 database matching compounds used for XRD analysis.

PDF number	Formula	Space group	Cell parameter ($\text{\AA}$)	Phase
01-071-7594	$CrNi$	Fm-3m (225)	3.590	γ
01-085-8671	$Ni_3(Al_{0.5}Ti_{0.5})$	Pm-3m (221)	3.586	γ'
01-070-2903	$(Cr_{0.2}Ti_{0.8})C$	Fm-3m (225)	4.299	MC
00-035-0783	$Cr_{23}C_6$	Fm-3m (225)	10.660	$M_{23}C_6$
01-083-3018	Co_3Mo_3C	Fd-3m (227)	11.070	M_6C

Figure 4.7 shows the XRD results for the samples subjected to HIP-annealing prior to standard heat treatment. It is worth noting that secondary matrix reflections associated to W-L α characteristic emission are visible across all diffractograms. This is attributed to tungsten contamination of the X-ray tube. Overall, results are consistent with SEM observations. A minor γ' peak is observed at $2\theta = 35.4^\circ$ in the diffractogram before

solution treatment (red), which is no longer visible after this step (blue). As mentioned before, due to the low cooling rate after the HIP step, it is not possible to ensure that the high temperature microstructure was retained, and therefore a posterior solutioning step was applied.

The biggest changes occur during the first ageing step, in which secondary carbide precipitation takes place. A minor peak linked to $M_{23}C_6$ is observed at $2\theta = 37.4^\circ$. This angle is slightly smaller than the PDF reference value of 37.7° . Nonetheless, this difference could be attributed to a non-stoichiometric composition, with possible presence of larger elements such as Ti and Mo increasing the lattice parameter and shifting the peak to lower angles. In the remaining samples under study, the position of the peak remained unchanged, which could indicate that carbide composition does not vary enough to produce a modification in its lattice parameter.

In accordance with SEM observations, there are no significant differences in the diffractogram before (green) and after the second step ageing (black). A minor peak possibly associated with primary MC carbides was also detected in all the samples.

Unequivocal identification of minor phases in XRD is limited by several factors: first, the reduced intensity of the peaks is in some cases close to the background noise level. Second, compositional changes may result in subtle modifications of the lattice parameters, that lead to a broadening of the peaks. In the case of γ' crystallite size also contributes to this phenomenon. Lastly, having multiple phases coexisting results in severe peak overlaps, where minor phases are completely covered by high-intensity matrix peaks. Nonetheless, by combining the information from SEM analysis, phase diagrams and XRD, it is possible to identify with relative certainty the different phases that constitute the microstructure.

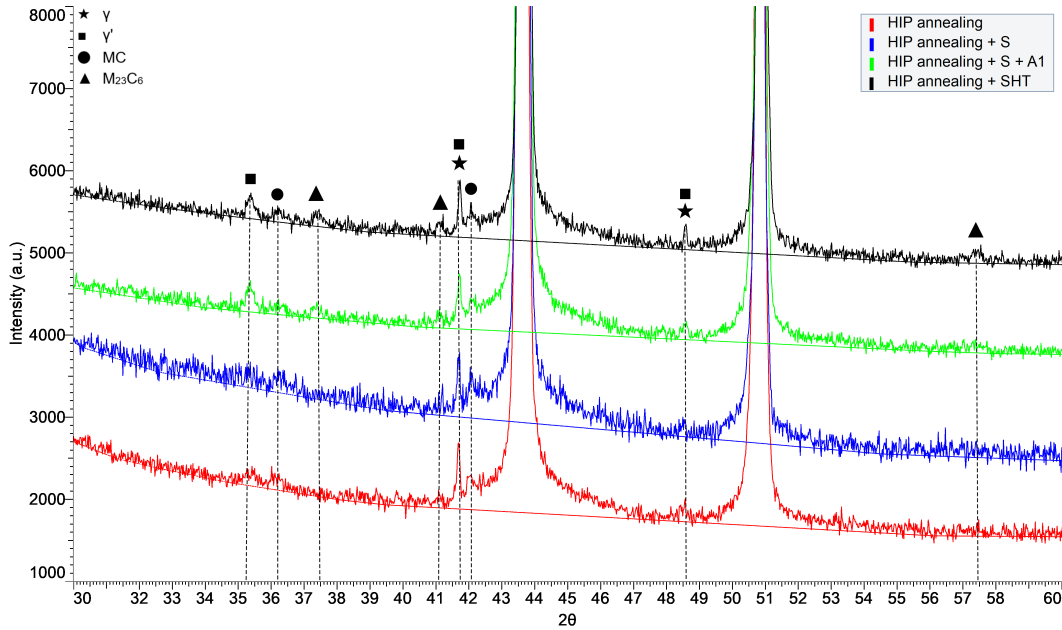


Figure 4.7: XRD diffractogram of HIP-annealed samples. The two major peaks correspond to γ/γ' and have been truncated to enhance the visibility of minor reflections.

A comparison of the fully treated microstructure obtained with and without HIP-annealing can be seen in Figure 4.8. Neither do the conditions show visual differences, nor did the quantitative analysis reveal statistically significant variations in precipitates size. As a result, it would be expected that the HIPed material shows better mechanical properties and reliability due to the defect healing nature of the HIP process.

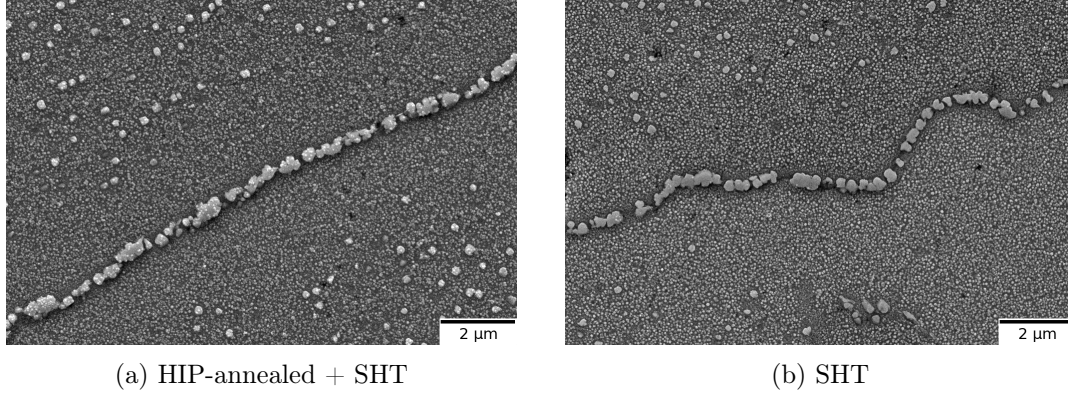


Figure 4.8: Microstructure with and without HIP-annealing post deposition treatment.

The alternative processing routes, combining multiple heat treatment steps with HIP, result in significant changes in the material's microstructure. Figure 4.9 shows the microstructure from the sample subjected to a combined HIP solutioning and first ageing. There is extensive presence of intragranular carbides, while only some of the grain boundaries exhibit carbide precipitation. Higher magnification images revealed that there is fine γ' present in the sample, that could have formed during cooling after the heat treatment. The smaller size of these precipitates compared to the ones observed after the conventional first ageing step could be attributed to the slower diffusion rates at elevated pressure during the HIP process [57].

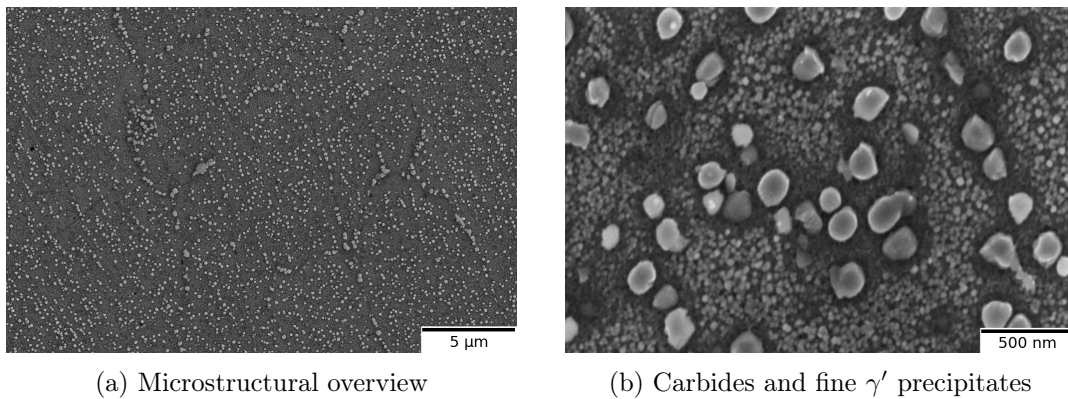


Figure 4.9: Partial CombiHIP sample microstructure after HIP solution and first ageing.

Figure 4.10 shows the comparison between sample 10, subjected to HIP solutioning and first ageing, followed by standard second ageing; and sample 14, produced through the complete CombiHIP route. In both cases there is a more continuous carbide wall along the grain boundaries. More extensive intragranular precipitation is observed in the partial

CombiHIP sample, that was already visible before the second ageing step. No significant differences were observed in γ' precipitates.

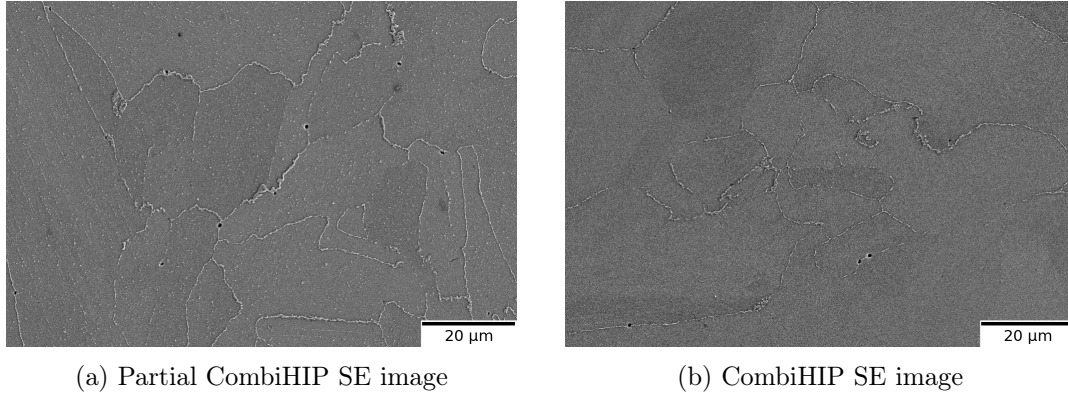


Figure 4.10: Microstructure after partial CombiHIP + A2 and CombiHIP treatments.

Figure 4.11 shows the XRD comparison of fully heat-treated samples obtained through the different routes. The four specimens exhibit peaks associated to the matrix γ , γ' , MC, and $M_{23}C_6$ carbides. As samples after the complete heat treatment contain a higher carbide fraction, it was possible to index more than one carbide peak, which makes the analysis more reliable. However, no peaks associated with M_6C carbides were detected.

As shown in Figure 4.12 the presence of M_6C was confirmed by means of BSE images paired with EDS analysis. The elevated Mo content in this phase results in a brighter contrast in BSE images. It is also visible that these represent only a minority of the carbides, which explains why they remain below detection limits of XRD. On the other hand, due to their elevated Ti content (see Fig. 4.13) MC carbides exhibit a darker contrast. Lastly, Cr-rich $M_{23}C_6$ carbides appear in a similar grey value as the γ matrix due to the similarity in the atomic number of their main elements. Furthermore, EDS spatial resolution is on the same order of magnitude as the carbides size, which in turn results in matrix interference during the measurements. For this reason, EDS was only used as a comparative tool to further reinforce the nature of the different carbides but can not be used for quantitative analysis of their composition.

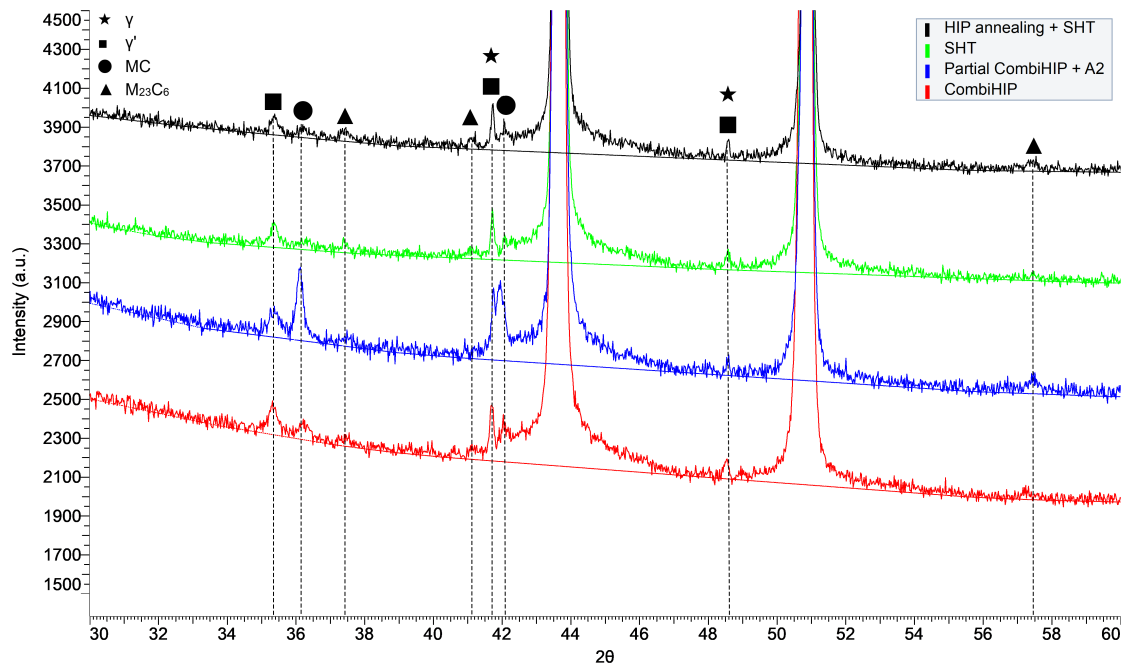


Figure 4.11: XRD diffractogram of fully treated samples. The two major peaks correspond to γ/γ' and have been truncated to enhance the visibility of minor reflections.

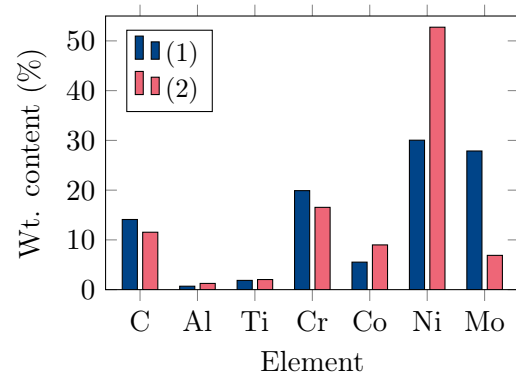
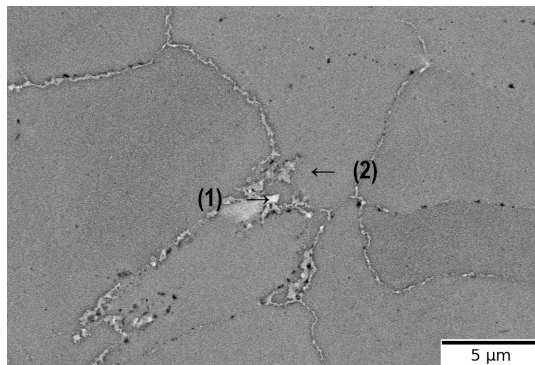


Figure 4.12: CombiHIP sample BSE image and corresponding EDS analysis. Note the high Mo content in the brighter spot.

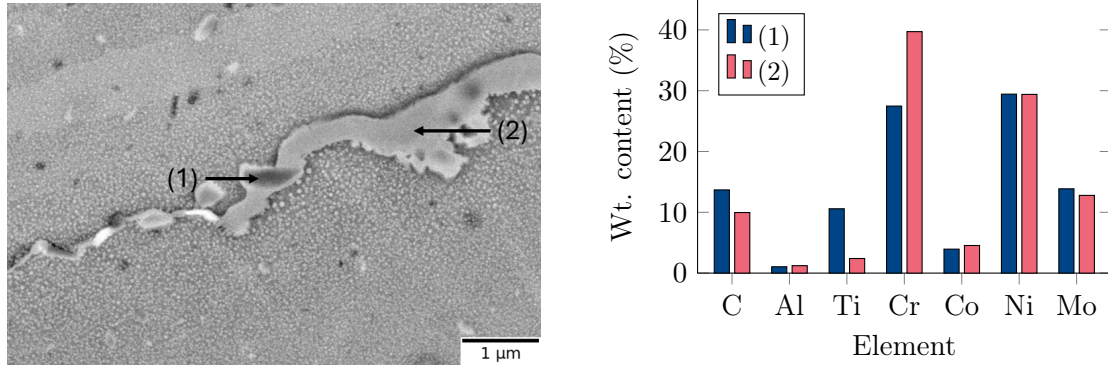


Figure 4.13: Partial CombiHIP sample BSE image and corresponding EDS analysis. Note the high Ti content in the darker spot.

A summary of the quantitative results from the different routes microstructural parameters can be found in Table 4.2. Regarding γ' precipitates, the largest were found in the HIP-annealed and SHT samples. On the other hand, both samples processed through the CombiHIP route resulted in 20% finer γ' , which could be beneficial to the material's mechanical properties. As introduced before, this could be related to the slower diffusion of elements under HIP high pressure. The higher standard deviation of the measurement in the HIP-annealed and SHT conditions reflects a bimodal distribution of γ' . Specifically, smaller particles in the 20 nm range predominate around the carbides, whereas larger precipitates, approximately 60 nm in diameter, are distributed throughout the rest of the matrix.

With respect to carbides, HIP-annealing and SHT samples showed no significant differences. The partial CombiHIP sample, instead, showed the biggest amount of carbide precipitation among all the conditions. Carbide morphology was also severely modified, from discrete particles in HIP-annealing and SHT to semi continuous walls in Partial CombiHIP and CombiHIP. Lastly, the CombiHIP sample showed 40% finer grain boundary carbides compared to Partial CombiHIP. This could be beneficial for the macroscopic behaviour of the alloy as thick grain boundary carbides can act as fracture initiation points [4].

Table 4.2: Quantitative microstructural analysis of fully treated samples from every processing route.

Processing Route	γ' diameter (nm)	GB carbides thickness (nm)	IG carbides diameter (nm)
HIP annealing + SHT	56 ± 15	250 ± 98	166 ± 32
SHT	52 ± 15	264 ± 71	167 ± 33
Partial CombiHIP	41 ± 11	253 ± 141	177 ± 33
CombiHIP	42 ± 10	170 ± 87	128 ± 16

4.2 Long term thermal exposure

4.2.1 Microstructural evolution

The LTTE cycles caused significant modifications in the material's microstructure. The aforementioned quantitative image analysis approaches were employed to quantify these effects. Figure 4.14 presents the results from γ' characterization. To put these values into perspective, an equal area region from each sample is shown in Figure 4.15. A transformation in the morphology of the precipitates was also noted, from spherical to cuboidal after the 850 °C and 930 °C cycles. This aligns with previous reports that link this phenomenon to a transition from a superficial energy-controlled to a strain energy-controlled process [1]. For small particles, total energy is dominated by interfacial energy and thus minimized by adopting a spherical shape. As particles coarsen, the misfit strain energy becomes dominant, which leads to a transition to cuboidal shape. Due to coherency with the matrix, preferential orientation of the precipitates was observed, with the crystallographic orientation relationship being $[110]\gamma//[110]\gamma'$ [13].

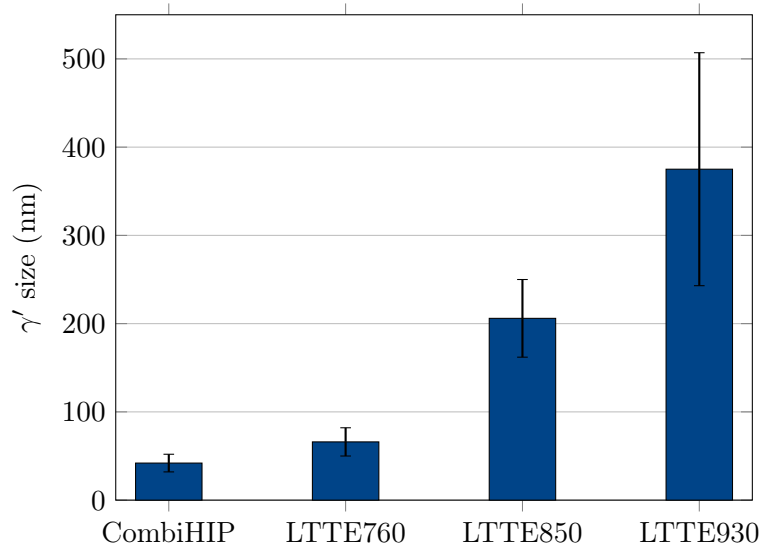


Figure 4.14: γ' size distribution results.

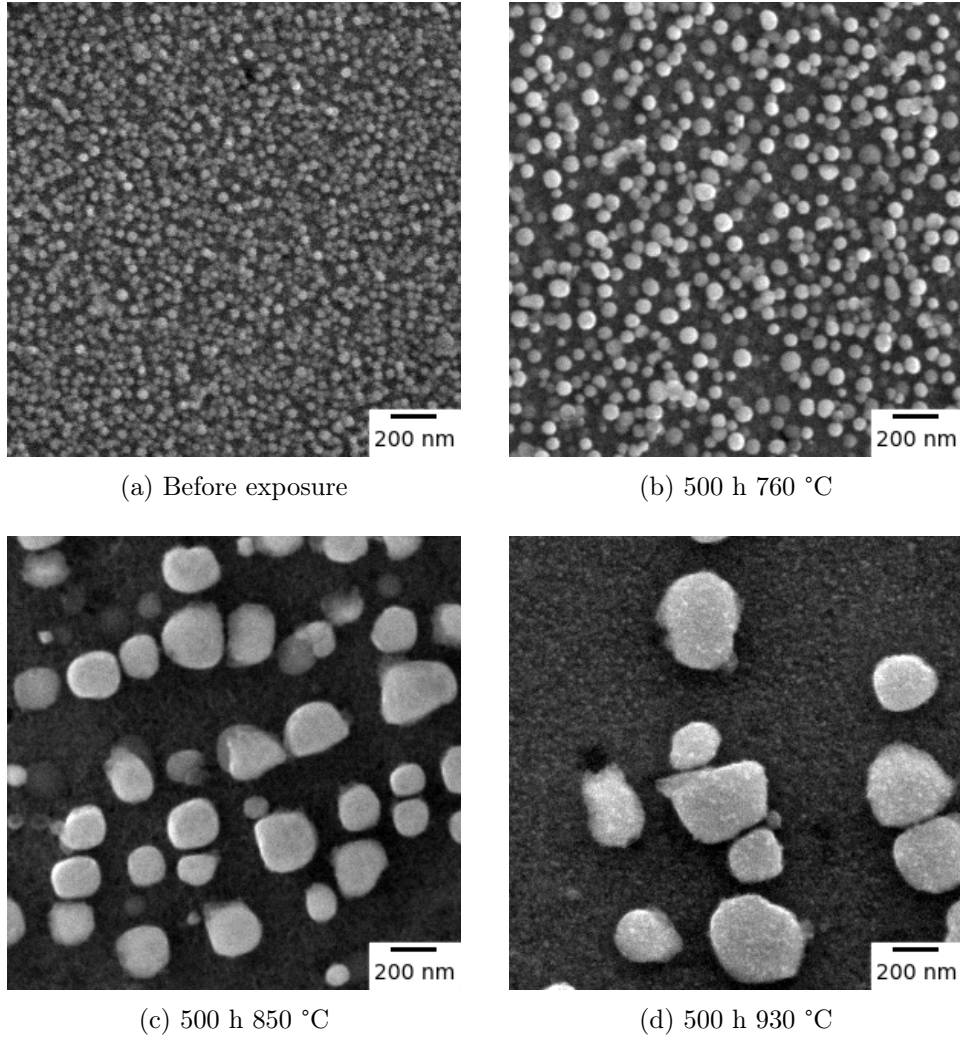


Figure 4.15: 40,000 $\times$ SE images cut-outs showing γ' coarsening.

Pronounced differences were observed in the carbides as well, that also coarsened during the exposure. The quantitative results are shown in figure 4.16 and can be visualized in Figure 4.17. Even though μ presence is predicted in the equilibrium phase diagram up to 800 °C neither μ nor any TCP phases were observed after any of the cycles. This is in line with existing literature, where reports of μ nucleation in PBF samples begin after 3000 h exposure at 750 °C [18]. The absence of this phase constitutes a further confirmation of the material's microstructural stability and is probably linked to kinetic constraints.

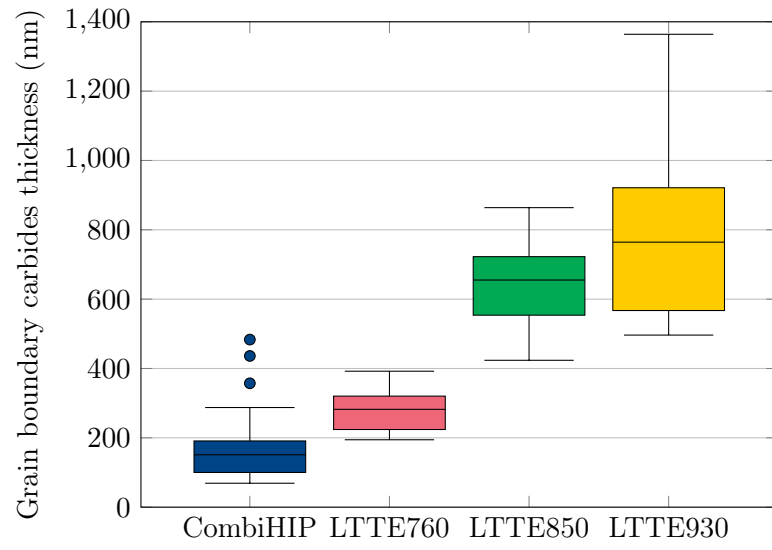


Figure 4.16: Grain boundary carbides size distribution comparison.

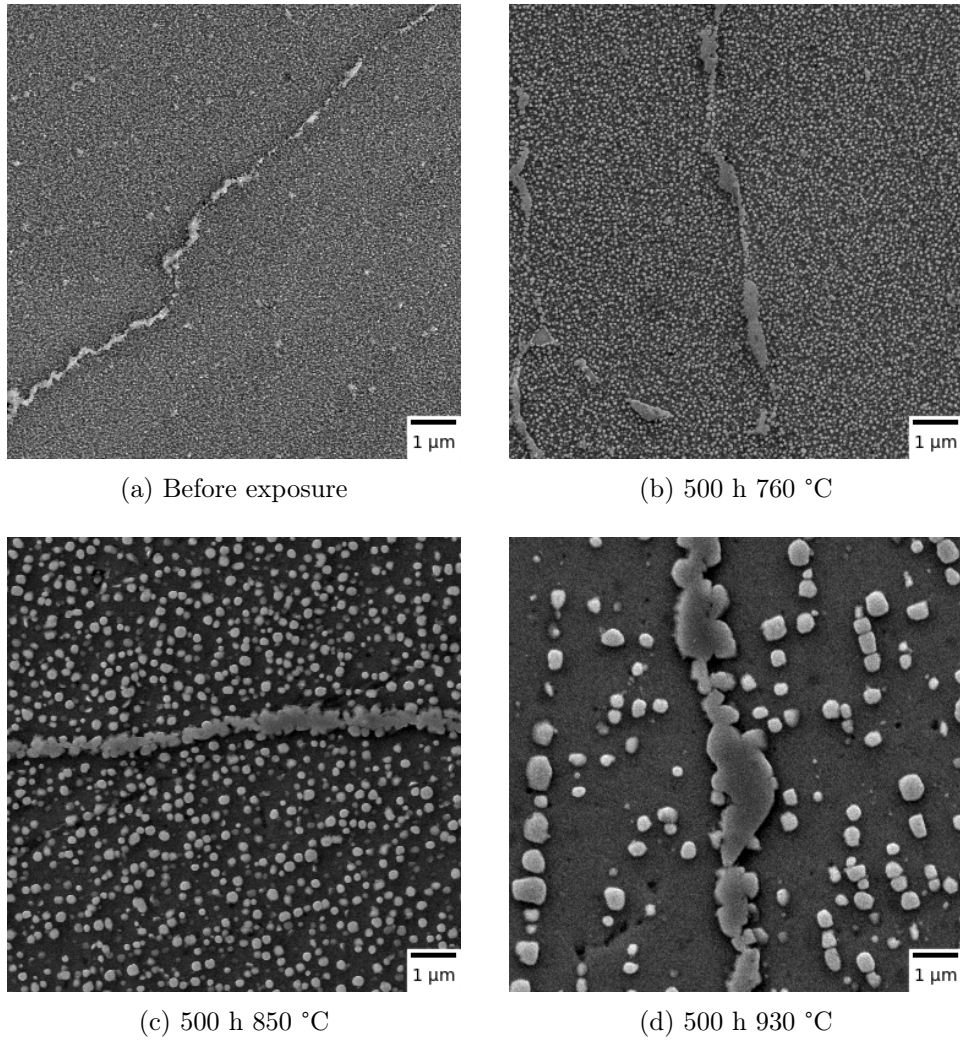


Figure 4.17: 10,000 × SE images cut-outs showing carbide coarsening.

The XRD diffractograms for these samples is shown in Figure 4.18. Minor phases peaks showed significant variations among the samples, in contrast to the higher intensity matrix peaks that remained mostly unchanged. $M_{23}C_6$ carbide peaks relative intensity increased with exposure temperature at the expense of primary carbides MC. This behaviour is in line with reported results and responds to the slow decomposition of primary carbides to produce secondary carbides and γ' [13]. Compared to wrought samples, primary carbides in PBF-LB samples are considerably smaller, often sub-micron in size. This, combined with the elevated exposure temperature could explain why primary carbide peaks are no longer visible after the 930 °C exposure cycle.

M_6C carbides have slower precipitation kinetics, as they require the diffusional flow of Mo. For this reason, in accordance to SEM observations, M_6C peaks are smaller and wider, which makes them difficult to differentiate from the background noise.

The unidentified peak at $2\theta = 41.8^\circ$ corresponds to the matrix and originates due to the presence of Tungsten contamination in the equipment, which results in W- $L\alpha$ characteristic X-ray emission.

Lastly, it can also be seen that γ' superlattice peak becomes progressively narrower with increasing exposure temperature. According to the Scherrer equation, peak width is inversely proportional to crystallite size. Therefore, as γ' precipitates coarsen, their peaks narrow. However, for precipitates larger than 100 nm, this effect is hindered by the instrumental width of the peaks.

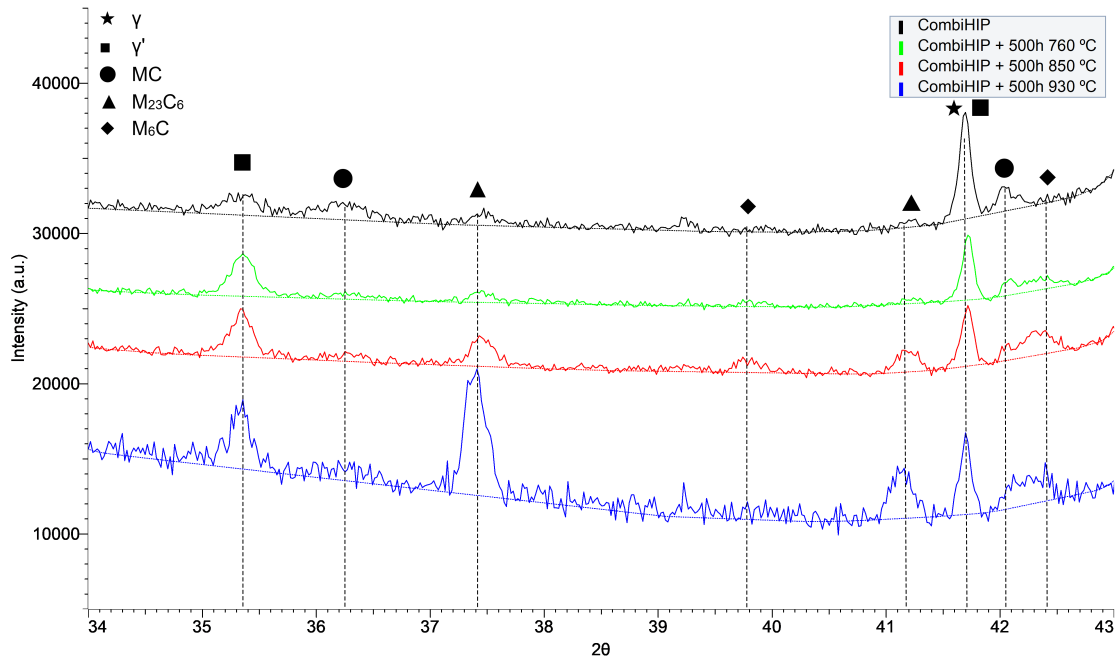


Figure 4.18: XRD diffractograms of LTTE samples. Amplified minor peaks region.

A summary of the quantitative results from the LTTE microstructural evolution analysis can be found in Table 4.3. Intragranular carbides could not be quantified for the samples exposed at 850 °C and 930 °C due to their similarity with the coarsened γ' particles.

Table 4.3: LTTE microstructural parameters evolution.

Condition	γ' diameter (nm)	GB carbides thickness (nm)	IG carbides diameter (nm)
CombiHIP	42 ± 10	170 ± 87	128 ± 16
LTTE 760	66 ± 16	289 ± 60	187 ± 55
LTTE 850	206 ± 44	643 ± 121	-
LTTE 930	375 ± 132	743 ± 270	-

According to Li et al. variations in the γ' – dislocations interaction mechanism can lead to transitions in the mechanical effects of coarsening precipitates. Up to 67 nm, weak-pair coupling interaction dominates and leads to an increase in Critical Resolved Shear Stress (CRSS) with γ' size. Above this point, strong-pair coupling dictates the strength, that slowly declines with γ' diameter. Finally, at 110 nm, a last transition to Orowan looping leads to a steeper decline in CRSS with precipitate size [18]. According to this, the sample exposed at 760 °C for 500h should have the highest value of strength, as it is just in the limit between weak and strong pair coupling mechanisms dominance. On the other hand, the other two samples have an average γ' diameter well above the Orowan bypass mechanism threshold, which would lead to a notorious decrease in strength.

Comparing the results with available literature on Haynes 282 LTTE, the 60 % increase in γ' after the 760 °C cycle is in line with the coarsening from wrought samples [17]. In accordance to published literature [18], an acceleration of the coarsening kinetics as a consequence of the higher diffusion rates was observed for the higher temperature cycles.

A similar trend was observed in the carbides' evolution. Literature reports state sub-micron carbides in heat-treated AM Haynes 282 [16] and studies on LTTE of wrought samples observed an increase in size and volume fraction during LTTE [17]. These phenomena have also been observed in the present study. As introduced before, due to the elongated interconnected morphology of the grain boundary carbides, the ellipse minor axis length (see Fig. 4.19) was selected as representative measurement from the thickness of the grain boundary carbide layer.

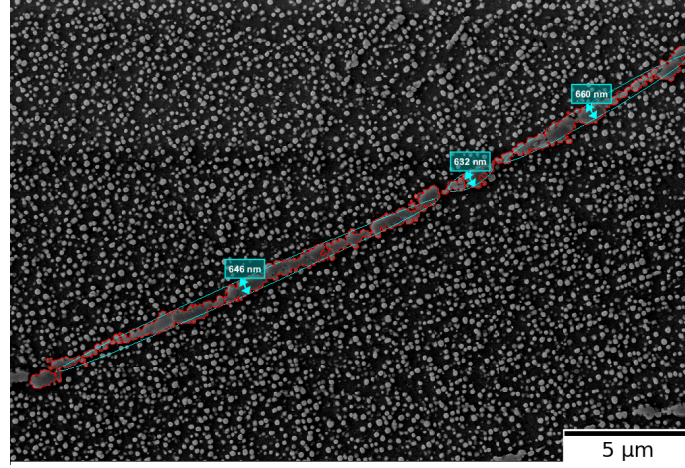
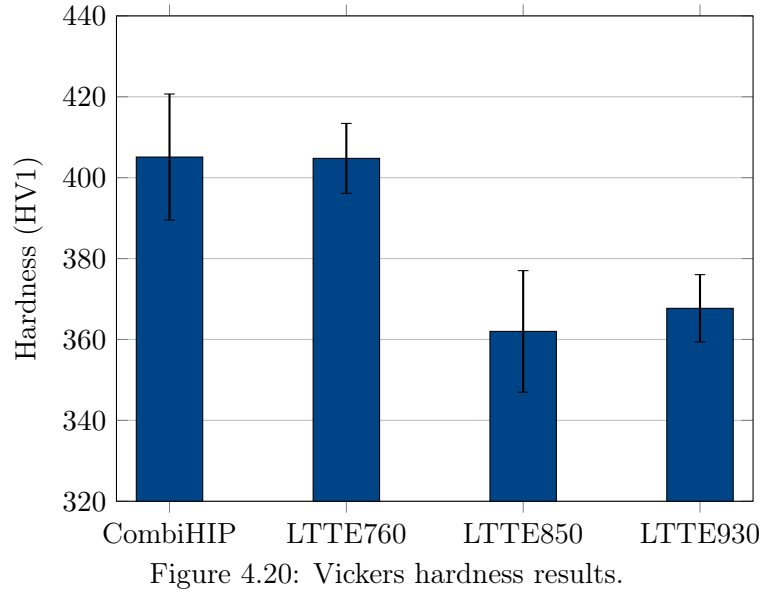


Figure 4.19: Grain boundary carbides segmentation results showing minor axis length size estimation.

The thickness of the grain boundary carbide layer increased in every cycle. A substantial difference was observed among the different conditions. While the 760 °C exposed sample exhibited a 70 % increase in size, the 850 °C and 930 °C samples showed a 280 % and 340 % increment respectively. This can not only be attributed to the increase in diffusion rate, but also possibly to the partial dissolution of primary intragranular MC carbides [13]. The presence of interconnected grain boundary carbides is often associated to a loss of ductility, as they constitute a preferential path for crack propagation due to their brittle nature [4]. This effect will be further discussed in the following section.

4.2.2 Mechanical testing

The results from Vickers Hardness testing are summarized in Figure 4.20. The 760 °C exposure cycle did not have an effect on the material's hardness. On the other hand, both cycles at 850 °C and 930 °C resulted in a 10% hardness decrease compared to the pre-exposure values. This is possibly linked to the aforementioned coarsening of the γ' precipitates, which was found to be much more significant after the higher temperature cycles.



The similar hardness values from the 850 °C and the 930 °C samples could be linked to the presence of secondary ultra-fine γ' (see Fig. 4.21) in the 930 °C exposed sample. Even though primary γ' is 80% larger in the higher temperature sample, this secondary precipitation could have a counter effect, turning the material stronger. The size of these precipitates was estimated in the 6–20 nm range. Nonetheless, it was found to be too small to be accurately segmented.

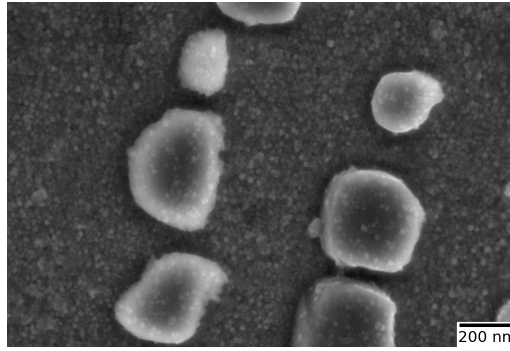


Figure 4.21: Primary cuboidal and secondary spherical γ' precipitates in the 930 °C exposed sample.

One possible explanation for the presence of bimodal γ' distribution is that it originated during the cooling stage after the thermal exposure cycle due to slow cooling inside the furnace. This phenomenon was only observed in the 930 °C exposed sample because at higher temperature the equilibrium γ' content is lower, resulting in a higher matrix supersaturation upon cooling, which increases the driving force for secondary precipitation. This hypothesis could be further verified by performing an accelerated cooling step (such as water quenching) immediately following the thermal exposure cycle to suppress secondary nucleation.

High temperature tensile testing was performed at 760 °C. According to the simulated equilibrium phase diagram for the nominal composition of the alloy, the γ' fraction at this temperature is 19.3 % [11]. As these are the main hardening precipitates in the material, their amount, size, distribution and interaction with dislocations play a fundamental role on its mechanical properties.

Modifications in the dislocation interactions with the matrix, precipitates, and among themselves, produce changes in the macroscopic properties of the bulk material. However, to observe this kind of phenomena, the use of Transmission Electron Microscopy is needed, which is out of the scope of the present work. Nonetheless, based on the previous reported work on this alloy, anti phase boundary coupled dislocation shearing dominates below 600 °C, Orowan looping above 760 °C and in between these two mechanisms together with stacking fault shearing operate simultaneously [11].

The stress-strain curves for the different conditions are shown in Figure 4.22. The results, summarized in Figure 4.23 are consistent with the reports from Shaikh et al. [39] and Swaminathan et al. [58].

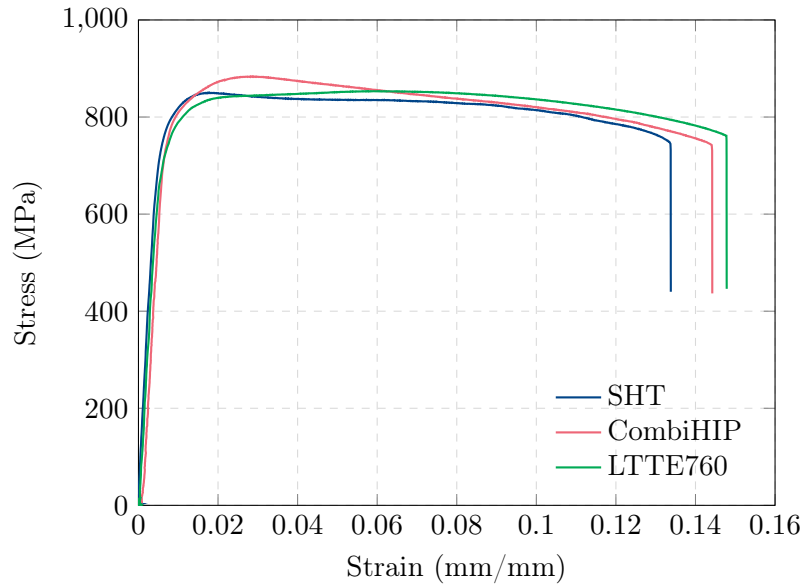


Figure 4.22: 760 °C stress-strain curves for different conditions.

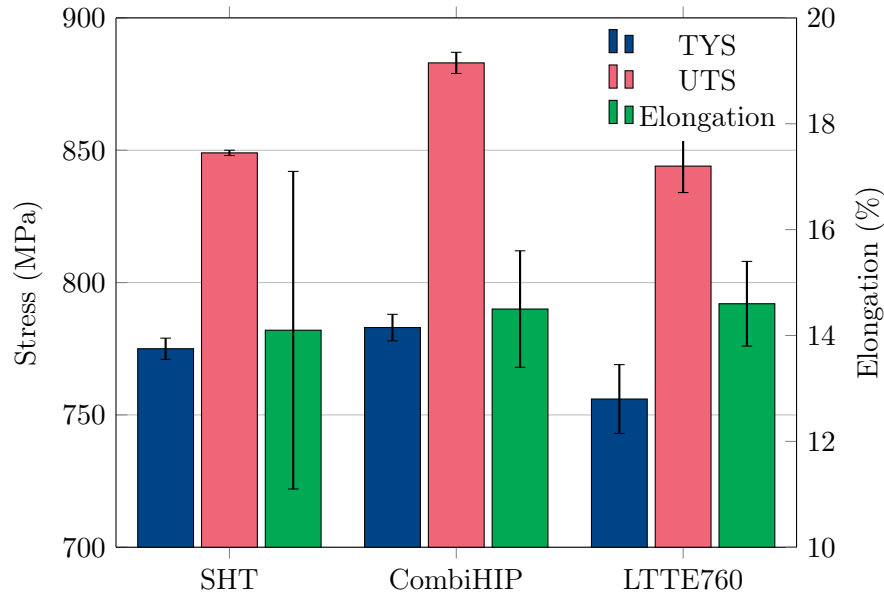
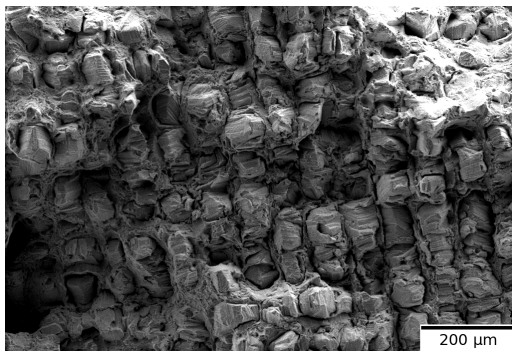
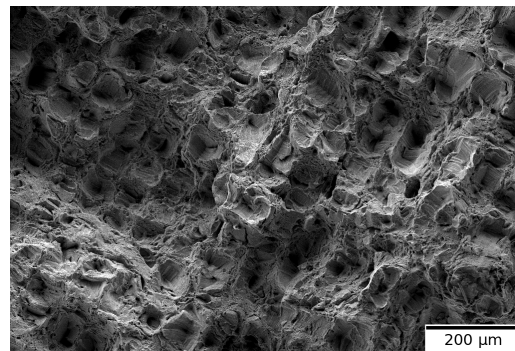


Figure 4.23: 760°C tensile testing results summary.

The CombiHIP treatment resulted in comparable mechanical behaviour to the SHT, with a minor 4 % increase in the UTS. The smaller dispersion of elongation values among the CombiHIP tests could be attributed to the defect healing properties of the process, that leads to more uniform samples [59]. Moreover, inspection of the fracture surfaces, shown in Figure 4.24, shows a better degree of metallurgical union among the grains, that can also be attributed to the HIP process. The similarity in mechanical properties and the aspect of the fracture surfaces suggests that the more interconnected grain boundary carbide network in the CombiHIP sample is not detrimental to the alloy's performance. This could be the result of a counterbalance effect due to the smaller size of both γ' precipitates and carbides.



(a) SHT



(b) CombiHIP

Figure 4.24: 760 °C tensile samples fracture surfaces.

LTTE of the CombiHIP samples produced a slight decline of both TYS and UTS, below 4 and 5 % respectively. At the same time, no significant differences were observed in the elongation. Even though significant γ' and carbide coarsening was observed in the SEM analysis after the exposure, these results indicate that the high temperature behaviour is

not sensible to these modifications. The similar aspect of the fracture surface, shown in figure 4.25 further reinforces this affirmation. Both specimens exhibit a mixed fracture, with zones characterized by ductile dimples and intergranular decohesion. Decohesion is linked to the presence of grain boundary carbides, which act as a preferential site for crack nucleation and propagation. Nonetheless, the presence of ductile fracture regions suggests that both grain and grain boundary strength is similar, thus leading to a mixed fracture. Higher magnification images reveal a similar dimple morphology and size, that probably originate in intragranular carbides or around γ' precipitates.

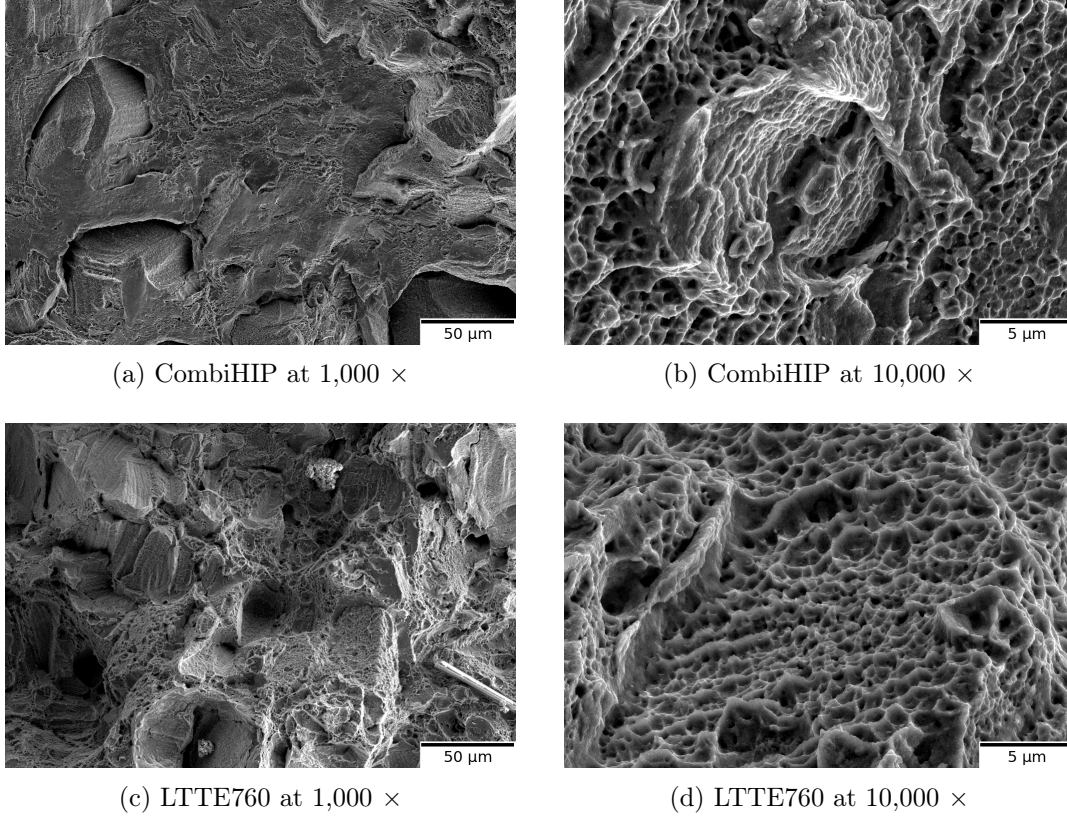


Figure 4.25: Fracture surface from specimens before (a), (b) and after (c), (d) LTTE.

Based on these results, it is possible to conclude that the CombiHIP treatment yields microstructural and mechanical properties comparable to those of the SHT. Moreover, it can significantly reduce processing time and improve reliability through defect healing. In addition to this, the long term thermal stability of the CombiHIP processed samples was validated in different exposure conditions, confirming performance retention up to 760 °C. The main outcomes from this project together with future research directions will be introduced in the following chapter.

Chapter 5

Conclusions

The requirement for high performance materials in the energy and aerospace industry simultaneously drives the advancement in alloy development and additive manufacturing techniques. In this context, it is critical to optimize post deposition treatments and to investigate the long term performance of AM superalloy parts for their adoption in such critical environments. This study addressed these challenges by evaluating the performance of an alternative heat treatment route for Haynes 282 superalloy, both in the as-treated state and after long term thermal exposure.

Different post-deposition treatments were compared for the fabrication of PBF-LB Haynes 282. The CombiHIP route, in which solutioning and two-step ageing are combined in a single HIP cycle, proved to achieve equivalent results to the standard heat treatment, while reducing processing time and taking advantage of the defect healing capabilities from the HIP process.

The effects of LTTE on CombiHIP processed samples were investigated and quantified under different conditions. The results from the 500 h exposure cycle at 760 °C indicate that the material holds its pre-exposure performance with no significant modifications. Even though coarsening of the microstructure was observed, the morphology and distribution of the minor phases was not altered, which in turn resulted in a good mechanical performance.

On the other hand, exposure cycles at 850 °C and 930 °C caused a transformation in the γ' precipitates morphology and more pronounced carbide coarsening. This translated into a hardness decrease that could also correlate with a decay in the tensile properties.

The microstructural evolution observed during the LTTE cycles highlights the necessity to test high temperature materials not only after their thermal treatment, but also after simulated service conditions. Although degradation kinetics may be slow at operational temperatures, accumulation over extended period of time can lead to significant differences in the mechanical performance.

The experimental results from this study confirm the suitability of Haynes 282 to produce high quality parts through additive manufacturing, specifically through PBF-LB. Moreover, by tailoring post deposition treatments, the efficiency of the process can be improved without negative effects on the mechanical properties.

Data from the LTTE cycles also confirms that Haynes 282 PBF-LB parts can withstand severe working conditions, up to 760 °C. Further studies on the mechanical properties after higher temperature exposure would be required to define the limit operation temperature for this material. Moreover, creep and fatigue test could be useful to fully understand the effect of microstructural changes on the performance of the material simulating different working conditions.

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