



Doctoral Dissertation Doctoral Program in Material Science and Technology (34<sup>th</sup> Cycle)

# Metallic powders production via Gas Atomization:

### Material development for Laser Powder Bed Fusion technique approach

By

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### Declaration

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\* This dissertation is presented in partial fulfillment of the requirements for **Ph.D. degree** in the Graduate School of Politecnico di Torino (ScuDo).

I would like to dedicate this thesis to my loving family and friends

## Abstract

Additive Manufacturing (AM) technologies have disrupted the production paradigm over the last ten years. Furthermore, this trend seems to be continuously growing and will lead AM to expand in the coming decades. Complexity for free high material yield and high mechanical performances concept. counterbalanced by low production rate and limited productive volumes, especially for the most used metal AM production technique: Laser Powder Bed Fusion Moreover, different boundary conditions require diverse material (LPBF). selection while a restricted materials palette is currently available. Material development for LPBF powder production needs a high cost and a tremendous amount of infrastructure. Gas Atomization (GA) is the most critical and widespread LPBF industrial powder production technology. Powder characteristics imposed by LPBF (shape, dimension, chemical and physical features) can be obtained only by GA production. However, GA plants are costly and difficult for researchers and academics to access. The GA and LPBF availability at Politecnico di Torino allowed us to overcome these technological limits. Thus, the LPBF production line has been studied since 2019 regarding non-commercial Al alloys composition development.

The first part of this thesis is focused on the GA plant installed in Alessandria. After a brief introduction to AM, LPBF and powder requirements, GA is described as AM powder production process. GA process parameters and theory were described to understand the process deeply. AISI 304L was chosen as benchmark product material for its low presence in LPBF scientific literature. 304L Powders were produced by GA using several atomization pressures. Chemical, physical and rheological tests assessed the atomization pressure effect on produced powders.

Moreover, produced powders' properties were compared to commercial products. 304L powders' feasibility for LPBF was then assessed. Single Scan Track (SST) approach was performed to identify a process parameter window for Concept Laser Mlab Cusing R.

An automated image analysis algorithm developed by our research group was used to recognize possible process parameters by on-top SSTs images. LPBF then produced 304L massive samples. The layer thickness effect was investigated concerning sample relative density. Finally, LPBFed sample properties were compared with traditional forming techniques samples ones.

Once the GA plant was tested and powders characteristics assessed, new Al alloy chemical compositions were developed. Firstly, commercial AlSi10Mg massive samples were produced and characterized. The scanning strategy effect on sample relative density was studied. AlSi10Mg was considered a reference material in our alloy design. AlSi10Mg and AISI 304L were mixed in several proportions to obtain two new Al-Fe rich alloys. AlSi8Fe9Cr2Ni and AlSi8Fe18Cr5Ni3 were produced using 1:4 and 1:8 304L/AlSi10Mg weight ratios, respectively. 304L was added both for Fe, Cr and Ni content. All these elements are used in rapidly solidified Al alloys for high-temperature strengthening. Fe and Ni precipitate in high-temperature stable phases, while Cr is mainly used to modify precipitation kinetics. 304L got a higher melting temperature than AlSi10Mg. When alloys are mixed, melting temperature varies as a function of the element composition. Consequently, volatile element content can be reduced in the melt. For this reason, alloys with very different melting temperatures can be atomized however the segregation effect must be checked. The atomization step was then performed avoiding chemical impurities and modification. After powder production, particles were characterized chemically and physically. Massive sample production was carried out on alloys while only AlSi8Fe9Cr2Ni was LPBF produced. Cracks and pores were evident in this alloy. LPBF feasibility was then improved by µ-TiB2 mechanical mixing to AlSi8Fe9Cr2Ni alloys. More than 99% of relative density was finally obtained. The first approach in GA alloy design was demonstrated with a new Al-Fe alloy composition.

# Introduction

Additive Manufacturing (AM) can be included as one of the most significant disruptive technologies developed since 80'. AM processes are divided into numerous types of technologies and their number is continuously growing. Historically, it can be categorized by the kind of material processed. Plastics and metals have been studied for years while composites and ceramics are increasingly getting attention. Many industrial sectors have been replacing traditional production techniques with innovative AM-based ones. This concept is especially true for high-value or high-impacted sectors (such as Aerospace, Oil and Gas, Racing and Jewellery) in which low production volume and high raw materials costs push for AM introduction. Many AM techniques are technologically mature and have already been introduced in previously cited working fields. However, some points of AM production process are still unknown. This thesis goal is to investigate some of that obscure points using a holistic approach over a complete AM process production, from raw material to Laser Powder Bed Fusion (LPBF) massive production.

The first part of the thesis aims to set up a complete view of the AM process, from the production of powders to their characterization and finally to their processability. A Gas-Atomization (GA) plant, installed in Alessandria's Politecnico campus, is studied for AM powder production. The characteristics of the plant and their effect on the powders' characteristics will be first evaluated. Secondly, GA products will be processed through an LPBF machine (Concept Laser Mlab Cusing R) to evaluate the products' bulk properties from the atomization cycle. The combined use of the GA plant and LPBF machine was performed to develop a new aluminum alloy composition.

The first chapter is focused on the state-of-art of LPBF production process. LPBF technique is modeled and described using a different kinds of process parameters. The main process parameters are evaluated from the final product's relative density. The most widespread model (Volumetric Energy Density or VED) does not provide a univocal correlation between process parameters and product relative density. Some important LPBF parameters (i.e. laser absorption coefficient or scanning strategy effects) are still undervalued and understudied.

Moreover, powder-related process parameters are rarely discussed in scientific literature. AM powder feedstock needs precise characteristics. For this reason, an overview of powder production techniques is performed. State-of-art powder production is carried out to evaluate the most suitable AM powder production process. Among all powder production processes, GA is unique for the obtainable powder features.

After assessing state-of-the-art additive and powder production processes, it was necessary to identify the working conditions in which the following thesis was developed. The second chapter analyzes the GA system present at Politecnico di Torino @ Alessandria Campus, a PSI Hermiga 100. Its components are described and studied. Plant design is discussed in order to understand GA peculiarities. One of the theoretical models for atomization particle dimensions control is investigated. Each GA process parameter that can influence powders' dimension is explained. In addition, the type of gas and production volumes needed outlined the GA process as a preferential choice. GA plant variables are discussed, focusing on how they can interfere with the desired results and how their variation can affect the characteristics of the final product.

In the third chapter, AISI 304L Stainless Steel is used as a benchmark product to evaluate the plant capabilities. The powders produced are analyzed from a chemical, physical, dimensional, morphological and rheological point of view to evaluate all the peculiar characteristics of a powder. This characterization will be carried out by exploiting several measurement techniques for each type of analysis to obtain a robust evaluation of the atomization process. In many cases, the properties of the powders produced can be compared with commercial powder products by GA or, where necessary, through other manufacturing technologies. This step is necessary to confirm the quality of powders produced in Politecnico's plant. They can, in all respects, be comparable to powders purchased through retailers on the global market. The die pressure analyses suggested a correlation between the atomization efficiency in the useful range for LPBF processes and the morphological characteristics of powders. Particle Size Distributions (PSD) are calculated using three methods: mass, volume and number. Comparing these different measurements is fundamental to understand powders' dimensional features correctly. Moreover, this comparison highlights another important powder aspect: particle relative density. Particle cross-section analysis and He-Pycnometry tests are performed to evaluate powders' % porosity. Morphological characteristics are essential for powders spreading during the LPBF process. GA particle shapes are compared to commercially Water-Atomized (WA) ones. A pronounced shape

variation is confirmed. Powders' high circularity can be associated with a remarkable ability to flow. Rheological aspects are investigated through a standard Powder Metallurgy (PM) test. Test results are consistent with commercial and scientific literature ones. XRD and SEM analysis allow the determination of several phases and observation of behavior during solidification of the alloy as a function of the dimension of particles. In addition, LECO and Quantometer tests are performed to identify any possible chemical outlier or impurity. Subsequently, the focus will be moved to analyzing the artifacts produced using the powder developed by GA. 304L LPBF process parameters have been optimized to reach a complete dense sample (more than 99 % relative density) starting from the scientific literature. Single-Scan Track (SST) approach is deployed for the first step of process window selection. Then, a fine-tuning SST defines a massive cube parameter process window. A comparison between two different layer thicknesses is performed and several optimal process parameters are reached. Also in this case, the XRD analyses will be used to evaluate the phases present within the artifacts. Moreover, phase composition will be related to the production process parameters for LPBF. The mechanical properties of the artifacts will be correlated with the microstructure obtained as a function of the VED.

In the second phase of the thesis, innovative compositions for an aluminum allow are analyzed, starting from AlSi10Mg alloy. In chapter four, new compositions are compared with the starting material to evaluate how chemical element variation influenced the overall properties of the final material. Powder compositional changes are costly and time-consuming. In addition, pre-alloying powders are necessary to avoid selective segregation of particularly mobile elements or the accumulation of elements in certain areas. Beyond these considerations, it is necessary to maintain high cooling rates  $(10^5 \text{ K/s})$  to extend the solubility limits as much as possible and to ensure the greatest possible spherical morphology of the powders to avoid spreading problems during the forming phase. An atomization plant used exclusively for the research and development of materials is the crucial point of this research. New composition AlSi10Mg-based alloys are pre-alloyed in the GA melt chamber and subsequently atomized. The final products are analyzed in both powder and bulk states. A different strategy for LPBF optimal processing is described. Ceramic micrometric reinforcing particles are applied as an inoculant agent for the complete densification of massive cubes.

The possibility of obtaining products of equal commercial quality makes it possible to develop and analyze new formulations of metal alloys. Rapid solidification processes do not follow equilibrium transformations and so cannot be studied by phase diagrams. Therefore, all the tools available to analyze the development of phases through equilibrium variation are not applicable in this field. This problem prompts us to reflect on two essential issues:

- Compositions obtained at 10<sup>5</sup> K/s solidification rates can be further optimized concerning new solubility limits (extension of the elements' solubility limits as a cooling rate function). It leads to the conception of new alloys with precipitates, phases and microstructures that are entirely different from those studied nowadays.
- There are currently no tools for evaluating the phases that form during composition modification at high cooling rates. Phase diagrams can help formulate which phases might occur via the meta-stability lines, but they are insufficient. For this reason, in recent years, analyses such as Scheil simulations have been increasingly used to evaluate which phases solidify in the event of lack of diffusion. However, a clear strategy for developing new metal alloy compositions has not yet been identified.

From this point of view, all the work and results obtained by this PhD thesis could be considered a first approach to the problem. With this work, it is demonstrated the possibility of producing and characterizing new chemical composition AM alloy. However, new composition development needs a robust theoretical method to formulate a rigorous formulation algorithm. In this sense, Artificial Intelligence, Big Data and Machine Learning applications in the material science field will grow more and more in the future.

"There's Plenty of Room at the Bottom"

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# **Chapter I**

# 1 Introduction to Additive Manufacturing

Additive Manufacturing (AM) is a set of technologies that has developed exponentially since the late 1980s. According to ASTM F2792-12, AM is a set of processes based on adding material to create a physical component from 3D model data, usually layer by layer [1]. Often, due to their peculiarities, additive technologies are opposed to subtractive technologies (like machining) and forming technologies (like deformation or casting processes) [2], although they may be used in conjunction with such processes to obtain functional components compatible with any industrial requirements [3]. In fact, in recent years, the industrial manufacturing sector has registered a growing interest in these technologies and their use has considerably increased. For this reason, the constant progress of technological know-how in the realization and use of AM techniques was developed in numerous application fields over the years. The technologies within the universe of AM are many and their number is growing day by day [4]. The current technologies can be categorized in several process families: vat photopolymerization (VPP), material jetting (MJT), powder bed fusion (PBF), directed energy deposition (DED), material extrusion (MEX), binder jetting (BJT), and sheet lamination (SHL) [5]. technologies can be found in their advantages. For example, greater design freedom, since this technology has the peculiarity of having less stringent design constraints than traditional forming techniques. For these

technologies shape complexity of the parts does not represent a limitation (often reported as the idea of "Complexity for free") [3].

Furthermore, it is also possible to create trabecular structures within the components. These structures give good mechanical properties and reduce the mass of components due to a high fraction of empty spaces within them. In addition, it is also possible to reduce the assembly operations and the number of parts of any assembly fabricating components capable of absolving the whole functions. An example of how these technologies can innovate an entire production sector is the ability to make conformal channels designed ad hoc to improve molding processes. Mold design needs to improve heat exchange in order to minimize production time. Heat exchange could be maximized using conformal channels. These channels (in which the cooling fluid flows) would be impossible to fabricate with traditional technologies [6].

Moreover, in many industrial fields, an additive approach allows for less material waste compared to subtractive technologies. Any removal of material is reduced to finishing operations only. AM also can implement topological optimization techniques, i.e., designing components in which the material is used where it is needed and validated through analytical simulations. Brackets, tools or molds' absence minimized instrumentation needs. Moreover, component customization can be greatly reduced in price. It is sufficient to modify the 3D design of the component according to the customer's needs. This aspect could be essential, for instance, in the case of biomedical applications like prostheses and anatomical implants [7].

However, these technologies also have some drawbacks. It is often necessary to insert supports, i.e. structures that support the product during the forming process. The number of supports needed for the production can even become a break-even point compared to other traditional technologies, mainly on high-value-added materials [8]. There are often difficulties in mass production caused by the small volumes of production chamber, particularly for powder bed technologies, i.e. hardly exceeding 0.5 m3. AM technologies are born to produce prototypes and, therefore, got the inherent characteristic of being discontinuous and challenging to adapt to mass production. Finally, there is still a limited choice of materials, caused mainly by the difficulties and costs of powder production, which is the most used form of raw materials. Despite this, an increasing number of companies and products have been launched into the global market during the last five years [4].

Considering previous statements, it is easy to understand how AM technologies can find applications in numerous sectors. For instance, in aerospace or racing fields, the necessity for better performances is not subject to economic constraints. In that cases, these techniques are perfectly fit to achieve highly competitive results. Polymers and metals remain the mainly investigated material categories in the industry. Nevertheless, ceramic materials are attracting increasing interest, for example in the civil construction industry. Considering AM techniques for metals and alloys, as listed in Figure 1.1, it could be stated that they are long-established.



Figure 1.1: Principal AM techniques currently used for metals [2]

In particular, with powders as starting materials, there are three leading technologies currently used to produce final components. They are divided into powder-bed techniques and powder-deposition techniques. The first case in Laser Powder Bed Fusion (LPBF) and Electron Beam Melting (EBM) artifacts are built by a layer-by-layer powder deposition on the building platform. Powder deposition techniques are normally referred to as Direct Energy Deposition (DED), applied mainly in large object repair (especially for aerospace and power generation). Some

wire variants (Wire-Arc Additive Manufacturing and Electron Beam Additive Manufacturing) that allow higher production volumes to be achieved were also developed. However, such technologies have not yet been widely explored. Nowadays, the most widely used technique in the production of metal components through AM is undoubtedly LPBF [4].

#### 1.1 Laser Powder Bed Fusion

Laser Powder Bed Fusion (LPBF), known also as Selective Laser Melting (SLM), is a powder bed fusion (PBF) technology in which the component is manufactured by melting the deposited metal powder. Powders melting is provided using either an Ytterbium (Yb) fiber laser or a YAG laser. The process is divided in several steps: powder is deposited by a recoater; the laser melts powders following the STL file, derived from the CAD geometry; the build platform drops one layer down equal to the layer set and powder is deposited again, and so on until the job is complete (Figure 1.2). Due to the process nature, the rapid passage of a concentrated laser on a powder-bed, extremely high cooling rate could be reached. As function of process parameters, cooling rate up to  $10^8$  K/s was demonstrated [9]. For this reason, LPBF has nowadays considered a Rapid Solidification Process (RSP) like melt spinning or copper mold casting. Thus, metastable phases and very fine microstructures with high mechanical performances can be obtained. The typical power range of laser fiber varies from 100W to 1kW, with wavelengths close to the infrared window and laser spot diameters between 50 and 100 µm. The construction chamber is filled with an inert gas, either Nitrogen or Argon, to avoid oxidation [10].



Figure 1.2: LPBF simplified scheme [11].

However, it is helpful to underline that previous considerations have a general value, as each manufacturer has implemented its system parameters to improve the final products. Therefore, it is necessary to carry out in-depth studies on individual machines, analyzing the process parameters and the strategies adopted to obtain the desired result. The main parameters that influence the LPBF process can be classified into four families, namely:

- related to Laser
- related to Temperature
- related to Powder
- related to Scanning Strategy

Depending on the desired focus, properties could be varied as a function of the process parameters. Typically, reaching a relative density as higher as possible is the main goal for initial trials. Once almost 99% of relative density is achieved, process parameters were adjusted in order to find the best compromise between relative density and machine productivity [12].

Historically, the laser-related parameters are the first studied: laser power (P) in W, scanning speed (v) in mm/s and distance between two consecutive laser tracks, called Hatching distance or  $H_d$ , in mm [9,13–15]. For example, at constant  $H_d$ , the

relative density of products decreases both when P decreases or when v increases. Usually, v parameter can vary between 100-7000 mm/s, associated with P from 90 to 400 W, at  $H_d$  between 0.06 and 0.2 mm. These values strongly depend on the characteristics of the LPBF machine.

In addition to these, there is a parameter that is strongly connected to powders: layer thickness (Lt) in mm, i.e. the distance between recoater and building platform/powder bed. Previous parameters are related to relative density through a complex parameter called Volumetric Energy Density (VED) which represents the energy density per unit of volume [J/mm<sup>3</sup>]

Relative Density = f (VED) = f 
$$\left(\frac{P}{v * H_d * L_t}\right)$$
 (1)

Thanks to the VED parameter is possible to compare material microstructures obtained by different sets of process parameters (P, v, Hd and Lt). VED is also related to machine productivity by an inverse relationship [12]. Excessively low VED does not make possible the phase transition to create liquid melting, thus causing the failure of the layer welding [16].

One of the less-studied process parameters is Layer Thickness. Although, in recent years, the scientific community has been focusing on  $L_t$  [17–19] its effect is still not completely clear.

Initially, some attempts were made to evaluate the powder layer production process using discrete element simulations [20,21]. Next, a correlation between simulations and experiments was evaluated to verify what was predicted by numerical model [22,23]. All these works, made it possible to obtain reliable spreading models that could be implemented on actual AM working conditions [22,24]. Notwithstanding, there is still a knowledge gap in the LPBF feasibility of alloys at different  $L_t$ .

However, VED is a simplified parameter for relating certain process parameters to relative density. For example, VED does not take temperature parameters into account. The temperature of the powder bed may influence, albeit slightly, the relative density of the samples. [25]. This result is achieved by the elimination of the relatively large pores produced in the case of high energy densities. In addition, the temperature of the powder bed affects the microstructure obtained from the specimens and the residual stresses. In aging samples, this can lead to over-aging and a drop in mechanical properties [26]. On the other hand, the use of a high-

temperature building platform could be compared to post-process stress relief, thus enhancing productivity (avoiding, in this way, a further heat treatment process).

Another issue related to VED adoption is the scalability among LPBF machines of different manufacturers. For example, Greco et al. [27], evaluate the transferability between two different LPBF machines of the same VED associated with a material with two different Particle Size Distributions. Similar VED values were obtained by modifying  $H_d$  and v proportionally. Nevertheless, no transferability was found, which means that it is always necessary to perform a new parameter optimization for each machine. In addition, the particle diameter influences laser absorption. With heat absorption modification, powders cool down and, consequently, change the final sample relative density.

Some approaches were studied to overcome VED formulation problems. The principal one is the introduction of new parameters inside the VED formula. Balbaa et al. [28] use the equation (2):

$$VED = \frac{K*P}{\nu*H_d*L_t}$$
(2)

where K coefficient (between 0 and 1 as value) considers the interaction between laser and powder. The higher the absorption coefficient (K), the lower the energy required for melting and evaporation. However, there are no more complex and universally accepted formulations for the correlation between process parameters and relative density for LPBF. Notwithstanding, none of these new formulations has included a parameter for scanning strategy correlation with relative density. The scanning strategy represents the way the laser passes over each layer. Different transformations on a 2D plane can be used to fill space. Symmetry operations are divided into operations on the same layer (exposure and scan pattern) and operations between consecutive layers (rotations and shifts). The choice of a given scanning strategy can also be made according to the presence of residual stresses [29] or desired growth of grains. Some attempts were proposed and analyzed experimentally during this work; they will be discussed in Chapter 4.

#### 1.1.1 Laser Power, Scan Speed and Hatching Distance

Among all VED parameters, laser power is the most studied and influential one [30,31]. Usually, it is varied together with scanning speed. While P and v are modified,  $H_d$  and  $L_t$  are kept constant. For example, Kempen et al. [32] was one of

the first study in which P-v parameters were investigated for AlSi10Mg. These experiments show how it is possible to obtain a good window of processability, with density greater than 99%, with a Concept Laser M1 machine equipped by 200 W fiber laser. P range between 170 and 200 W and v range between 700 and 1700 mm/s were investigated. An H<sub>d</sub> of 0.105 mm was kept constant. Results are showed in Figure 1.3 [32].



Figure 1.3: Process window modification as laser power and scan speed increase, by Kempen et al. [32].

As P increases, v increases to reach the optimal grade of densification. However, higher relative densities could be reached using lower P. The relative density values, closest to the ideal 2,68 g/cm3, are obtained with several VED values.

However, at higher energy densities, overall porosity increases. As demonstrated by Trevisan et al. [9] with EOS M270 machine (200 W as nominal laser power), this phenomenon happens when unstable melt pools are produced due to high VED values. In AlSi10Mg case, there is an excess of a liquid phase formation and the vaporization of the material. These phenomena resulted in an incorrect solidification path and "keyhole" pores formation. This fact implies a pores % increase once passed the VED processability window, as can be noted in Figure 1.4



Figure 1.4: Once the optimal VED value is reached, keyholes pores formation start, as stated by Trevisan et al [9].

Numerous experiments have established the influence of v on the densification of samples during the LPBF process. Scan speed variation can modify pores quantity and morphology as illustrated in Figure 1.5 from the study of Aboulkhair et al. [14]. As expected, with increasing v value, samples relative density decreases due to a decrease of VED.



Figure 1.5: Scan speed influence at a) 250 mm/s, b)500 mm/s c)750 mm/s d)1000 mm/s [14].

In order to investigate scan speed influence, Aboulkhair et al. [14] set H<sub>d</sub> (0.1 mm), P (100 W) and L<sub>t</sub> (0.04 mm) constant while v was increased: as can be seen in Figure 1.5, there is a decrease in relative density as v increases. Moreover, a modification of pore morphology arises. Also, in this case, insufficient energy caused a lack of particles to melt and consequently "Lack of Fusion" pores formation. Consequently, "Lack of Fusion" pores are much bigger than gasentrapped pores and ordinarily full of un-melted particles as shown in Figure 1.6 [13].

Although even reducing v, some pores were maintained. Gas (especially H2) is frequently entrapped during the solidification of the melt pool. Therefore, gasentrapped pores are more spherical and regular (Figure 1.5.a) [14].



Figure 1.6: SEM analyses of Lack of Fusion pores cross-section; un-melted particles are stacked inside pores [14].

Moreover, they Aboulkhair et al. [14] investigated the effect of increasing the  $H_d$  in massive samples' relative density. An increase of H<sub>d</sub> is related to an increase in porosity, in particular between two consecutive laser scans, as showed in Figure 1.7. These porosities are produced due to the reduced overlap between scan traces. The more the spacing increases, the more gaps are created, producing less relatively dense samples. This effect is most pronounced when the scanning strategy is

unidirectional, as can be observed in Figure 1.7.



Figure 1.7: In unidirectional produced samples, relative densities decrease as  $H_d$  increases [14].

Process accelerating could be achieved by using large  $H_d$ . However, to ensure high relative density components, lower  $L_t$  values need to be used. Therefore, samples need to be subdivided into a more significant number of layers, which means an increase in production times. Consequently, a compromise needs to be found between  $H_d$  and  $L_t$ .

#### 1.1.2 Layer Thickness

Lt is a powder-related process parameter representing the distance between recoater and building platform/powder bed, as already stated. It is strictly correlated to Particle Size Distribution (PSD) and, for this reason, LPBF systems usually vary between 15 and 60  $\mu$ m. It represents the height of each layer and, thus, the total number of layers depends on the L<sub>t</sub> values. Consequently, an increase in L<sub>t</sub> corresponds to a decrease in production time. Shamsdini et al. [33] compared the effect on mechanical properties of two different L<sub>t</sub> for the fabrication of MS1 steel by LPBF. They used an EOS M290 machine with a 400 W Yb-fiber laser with a
spot size of 100 µm to produce samples with 40 and 50 µm Lt. Relative density and Vickers micro-hardness (HV) were evaluated for 40/50 µm samples comparison but almost no difference was noted. A slight improvement in relative density and HV was noted for lower Lt samples, while a significant increase in production time was obtained. These findings were confirmed on Inconel 718 by Sufiiarov et al. work [34] which stated that strength properties are lower at higher Lt. At the same time, plasticity is higher concerning samples produced by lower Lt. The reason could be explained as in lower Lt, all the powders were fully melted and filled in between the powders' gap. Moreover, gas trapped is easier to be removed due to the less volume to travel inside a liquid phase. In addition, finer grain structures were achieved with smaller  $L_t$  [17]. However, VED is inversely related to  $L_t$ . As a result, decreasing VED is correlated to a decrease in the relative density of samples. Moreover, in recent study Jansen et al. [35] modify Lt definition dividing it into nominal and actual Lt. Nominal Lt could be defined as the height difference between recoater and building platform. However, it corresponds to actual Lt just for the first layer.



Figure 1.8: After exposure, powder layer height is modified by powder densification. Due to this fact, nominal and actual  $L_t$  converge just for first layer case. However, after 6-10 layers, steady state actual  $L_t$  is reached [35].

As illustrated in Figure 1.8, due to the consolidation of the powder material during melting, the effective powder layer height deviates from the nominal layer thickness after exposure. A steady-state could be reached after 6-10 layers. This way, actual Lt should be used in the VED formula to calculate the total energy quantity available to particles for melting. For actual Lt measuring, ad-hoc samples should be designed and manufactured in each job [35].

New VED concepts must be developed in future research to better understand the LPBF process.

### 1.1.3 Scanning Strategy

In addition, new VED concepts should be affected by a scanning strategy parameter. As already mentioned, the scanning strategy mainly affects the growth of grains, the presence of porosity and residual stresses. Nonetheless, it also affects relative density in LPBF samples. Depending on the desired result, it is possible to modify the scanning strategy to get the sample with the proper characteristics. The scanning strategy could be considered a set of 4 main scanning characteristics.

The scan pattern represents how the section of the sample is exposed. It could be considered the ratio between the scan vector e the total dimension of the layer. The main LPBF scan patterns are full (Figure 1.9.a), in which the laser melts the whole layer continuously; stripe (Figure 1.9.b), in which the laser melts the layer following defined stripes; and islands or chessboard (Figure 1.9.c), in which the layer is divided in squares of predefined size. For example, Island is GE Concept Laser default scan pattern, while stripe is the EOS one.



Figure 1.9: Examples of scan patterns for GE Concept Laser. a) Full scan pattern. b) Stripe scan pattern and c) Island or chessboard scan pattern. Adaption from [36]

The exposure represents the laser scan vector. For example in GE Concept Laser systems it can be modified as follows: 1D (Figure 1.10.a), that is the laser always maintains the same direction and, once a track is finished, it switches off, goes back, moves one hatching distance and restarts to expose; 2D (Figure 1.10.b), in which the laser changes the direction of 180° between one track and the next one, turning off to change the direction; and finally meander (Figure 1.10.c), that is the laser

changes direction of 180° between one track and the next one, but remains continuous during the change of direction.



Figure 1.10: Examples of GE Concept Laser possible exposure parameters. a) 1D. b) 2D and c) Meander. Adaption from [36]

The rotation between layers represents the rotation angle between two consecutive layers (Figure 1.11.a). For example, in GE Concept Laser systems it could be  $0^{\circ}$ , so there is no rotation between layers,  $90^{\circ}$  or  $67^{\circ}$ .

Finally the layer shift represents the distance of virtual plane translation between two consecutive layers (Figure 1.11.b). For example, in GE Concept Laser it could be set from 0.1 to 1 mm.



Figure 1.11: GE Concept Laser rotation scanning parameter. a) rotation between layers and b) shift between layers. Adaption from [36].

Even if scanning strategy is an essential parameter, it can be unknown before the microstructural analyses. It is possible to evaluate some of the effects cutting bulk samples into different sections. In Figure 1.12 by Thijsa et al.[35], it is possible to notice the different aspects of the melt pools according to the examined plane. The melt pool is the interaction of powder volume with the laser. It is normally represented as a half ellipsoid extruded along the scanning direction. In Figure 1.12.a) it can observed the x-y plane with an on-top microstructural visualization. Red arrows highlight the laser starting point. In the point in which the laser was turned on, melt pools are more extended and have probably welded more layers together. Traces are parallel each other and this could indicate Full 1D scanning strategy. Figure 1.12.b) and Figure 1.12.c) illustrate the y-z and x-z planes, respectively, in which traces are parallel overlapped. In the y-z plane as a side view, in the x-z plane as a front view, the typical melt pools shape as fish skin flakes superimposed along the building direction.



Figure 1.12: example of AlSi10Mg microstructures along different planes. a) x-y plane; b) y-z plane, c ) x-z plane and d) axes references [37].

## **1.2** Powder Requirements for LPBF

In the LPBF process, the starting material is represented by metal powders. As mentioned above, the properties of the finished product are a function of the characteristics of the raw material. In particular, several parameters primarily influence the process at the powder level. They are mainly shape, size, particle size distribution (PSD), chemical composition, melting temperature and absorbance. The powders can be spread and pushed by a doctor blade, also called a roller coater or recoater, without difficulty. This property is called "spreadability" and is associated with a high degree of compactness of the powder beds. It is responsible for the creation of dense parts once the particles are melted [9].

In order to obtain a compact powder bed, particle size distribution must comply with process requirements. Generally, particle sizes for LPBF must fall in a range between 15 and 63  $\mu$ m. As shown in Figure 1.13 [36], commercial powder samples of AlSi10Mg could include particles outside this range. Indeed, 15-63 is an ideal reference, as a broad particle size distribution causes smaller particles to occupy the gaps between the larger ones. However, a large amount of microscopic particles has two opposite effects. Firstly, fine particles form clusters more extensive than 80  $\mu$ m and, consequently, larger than the standard height of a layer. This first phenomenon could lead to inhomogeneity of the layer thickness [38]. The second undesired phenomenon is that it could inhibit an excellent spreading behavior of the powder itself.



Figure 1.13 FESEM image of AlSi10Mg powder by gas atomization process and sold commercially. The particle size distribution is centered in 15-63  $\mu$ m range, however smaller dimension particle could be observed as satellites [38].

In addition, powders chemical composition needs to be investigated before the LPBF process. Impurities could contaminate particle surface and bulk properties. In particular, oxide layers can modify the viscosity of the melt and can create defects inside bulk samples. Moreover, pores within particles can cause a higher porosity in final products, therefore decreasing their mechanical properties [9,39].

Currently, there is no single parameter for evaluating the quality of AM powder. Several powder parameters have been evaluated in the literature for years to determine whether a powder is good or bad for the LPBF process, being new or recycled [40]. As such, the quality of an AM powder can be assessed through two requirements in order to be processable: spreadability and powder-bed bulk density

### 1.2.1 Spreadability

*Spreadability* is the characteristic of powders to be deposited uniformly over a platform without voids or heaps creation [41]. It is an extrinsic property as it depends not only on intrinsic material parameters, such as true density or electrostatic surface charge of the particles, but also on extrinsic parameters such as size or morphology and their distributions, particle size distribution and particle morphology distribution, respectively. In scientific literature during recent years, efforts have been made to develop different approaches for the evaluation of powder beds with in-situ analysis, such as optical microscopy, computed tomography or thermography on samples of laid powder with subsequent image analysis [41–44]. These in-situ monitoring devices are already largely incorporated in newly developed LPBF machines in order to obtain a real-time evaluation of the spreadability phenomenon [45–48]. The scientific community is more and more careful on this topic, as can be further seen through the number of new papers published in recent years (Figure 1.14).



Figure 1.14: Scopus quantification of papers during last 10 years; keyword used TITLE-ABS-KEY (Powders) AND TITLE-ABS-KEY (Spreading) AND TITLE-ABS-KEY (Additive Manufacturing). Last seen on Scopus: 3/22 [49].

### 1.2.2 Powder-bed bulk packing density

*Powder-bed bulk packing density* is the characteristic of the powders to compact in the platform (i.e. to occupy as little space as possible under the same process conditions) and to create powder bulk compacts that require as little energy as possible to be fully melted. Also in this case, it is an extrinsic property as it depends not only on intrinsic material parameters, such as true density or electrostatic surface charge of the particles but also on extrinsic parameters such as size or morphology and their distributions, particle size distribution and particle morphology distribution, respectively. In scientific literature, it is a particularly well-studied property as it has historically been used in powder metallurgy processes [2,50–53]. It is the essential quality for a powder to fill a mold or a can. From this point of view, literature is full of references to the tap density or packing density of powders [17,54,55] but these characteristics are not entirely representative of a powder bed system. The boundary conditions for spreading, such as the platform size, affect the local compaction of the powders [20,56,57]. For these reasons, several approaches to evaluate powder bed packing density by creating ad hoc samples for on-site powders assessment were developed during the last decade [58].

These two characteristics oppose each other since an increase in spreadability necessarily implies a decrease in powder-bed bulk density. For example, an increase in the percentage of particles with a tiny diameter, i.e. a decrease in the  $D_{10}$  and  $D_{50}$  of the particle size distribution, implies better compaction of the powders as the empty spaces created by the coarser particles are filled by, the smaller ones [54,59].  $D_{10}$ ,  $D_{50}$  and  $D_{90}$  are peculiar PSD values, representing diameters of 10 %, 50% and 90% of the particle population. The chapter "Analytical Methods" provides a detailed PSD explanation. However, this could lead to agglomeration of the powder, which obstructs its distribution on the platform. At the same time, a denser powder compact will require less energy per volume unit (VED) to produce higher density products; finer powders will require less energy to pass into a molten state and fewer voids to fill during the transition to a liquid state prior to re-solidification [31,60]. As a result of an optimal powder packing density, it could be obtained a relative powder bed density higher than 60 %.

### 1.2.3 Definition of powder main requirements

LPBF powders need well-defined characteristics that guarantee a trade-off between the previously stated features. Therefore, these characteristics could be summarized as follows:

- A particle size distribution between 15 and 63 µm to guarantee adequate flowability, high bed bulk density and low melt energy per volume unit.
- A morphology as close to sphericity as possible to avoid inter-locking between particles and thus ensure spreabability.
- Low chemical impurities and lack of surface oxides, in order to obtain a product with low defects and high microstuctural homogeneity.
- Absence of powder porosity to increase the relative density of the powderbed and avoid interruptions in production.

## **1.3 Powders Production**

Several techniques were developed during the XX century to produce powdered materials as a function of particle requirements. As a consequence, different needs impose different production technologies. Shape, dimensions, and specific surface or chemical composition could be crucial factors for powder production technology discerning.



Figure 1.15: Examples of micrographs of powders from different production techniques. a) Hoeganas chemical process sponge iron-reduced ore; b) electrochemical deposition of Cu; c) Mechanical milling of Al alloy; d) Water atomization of iron powder and e) Gas atomization nickel alloy; adaption from [61].

In Figure 1.15 taken by the monograph of Lawley, various kinds of particles are represented. They are very different in shape and size and could be used for different scopes. In Figure 1.15.a) e b) for example, chemical and electrochemical processed powders are showed. In the first case (Figure 1.15.a) sponge iron-reduced particle is produced by chemical reduction of iron oxides with carbon and hydrogen. This technique produces powders with high internal porosities and "spongy" appearance as can be seen in Figure 1.16 b), as reported by Chasoglou [60].



Figure 1.16: Shape and Cross-section analyses of water atomized and chemical produced powders. As can be seen, even if similar shape could be reach, a great amount of pores are produced by chemical process; adaption from [62].

By contrast, dendritic-shaped particles could be obtained by electrochemical approach as illustrated in Figure 1.15.b). However, particle shape and dimension are unfit for LPBF. Grinding and milling processes were performed to produce particles in Figure 1.15.c). As can be noted, they presented a wrinkled and fragmented surface resulting from the cracking and fracturing of massive blocks in gradually decreasing size. Their complex shape gives them high inter-locking and friction abilities. As a result, high relative density and green strength could be achieved. On the other hand, interlocking and friction phenomena strongly decrease powder flowing behavior and prevent their use in the LPBF field. Moreover, due to the enormous amount of energy dissipated during the process, it is energetically unsuitable. In Figure 1.15.d) a Water-Atomized (WA) steel particle could be

observed. Compared to the chemical produced one, the particle morphology is still wrinkled and fragmented but it is less porous (Figure 1.16 a). In addition, WA powders are normally produced in LPBF size range. Finally, a Gas-Atomized (GA) Nickel alloy particle is illustrated in Figure 1.15.e). As evident from the marker, the diameter is about 40  $\mu$ m, and the morphology is perfectly spherical. From an initial analysis, it is possible to establish that atomization seems to be the most suitable process for producing metal powders for LPBF.

### **1.3.1** Atomization

*Atomization* is a powder production technique based on the concept of breaking a liquid film. Generally, a liquid bulk with a certain mass and surface is powdered by applying energy during the atomization phase. A tremendous amount of energy is needed for small particle surfaces formation, as can be seen in Figure 1.17. For this reason, atomization is an energy-inefficient process. However, it produces powders with unique characteristics.



Figure 1.17: From bulk liquid to powder formation, a great quantity of energy need to be used for surface creation; adaption from [63].

Four main physical principles could be used for atomization, as showed in Figure 1.18:

a) One-Fluid Atomization in which the metal melt is breakup by a *stimulus*, *like a vibration or an electrical impulse*. Low disperse PSD is obtained, but only coarse particles could be processed (> 200 μm).

- b) Two-Fluid Atomization in which the metal melt is breakup by a second fluid, gas or liquid. This atomization could produce powders as tiny as 10 μm or less. The difference in *kinetic energy of the two-fluid* is the main force that dominates the process.
- c) Centrifugal Atomization, a melt film, is cast on a rotating surface and divided into a particle by *centrifugal forces*. In this case, angular velocity is the key to process control.
- d) Vacuum Soluble Gas Atomization in which *negative pressure* is imposed by gas for the melt rising from the nozzle. Gas must be soluble in the metal to avoid any gas-trapping inside the particles.



Figure 1.18: Four main physical principles are used for atomization. a) One Fluid atomization; b) Two Fluid atomization; c) Centrifugal atomization and d) Vacuum Soluble Gas atomization; adaption from [63].

Many other techniques were developed during the XX century. Nevertheless, just some of these are commercially used for LPBF powder production. The main LPBF powder production techniques will be exposed in the next paragraph.

### **1.3.2** Main Atomization Techniques for LPBF powder production

#### 1.3.2.1 Centrifugal Atomization

Centrifugal Atomization (CA), also called rotary atomization, uses a surface in motion with a well-defined angular velocity to spread a film of metallic melt outside the surface and atomize it. As Yule and Dunkley [61] described, powders could be produced in three different regimes as a function of melt flow rate and angular velocity. In Figure 1.19, the three CA regimes are detailed: direct droplet, ligament, and sheet.



Figure 1.19: Three different CA regimes. a) Direct droplet regime; b) Ligament regime and c) Sheet regime [63].

Figure 1.19 a) shows the direct droplet regime. In this regime, the PSD tends to be mono-dispersity while a low production rate can be achieved. As the melt flow rate increases at a fixed angular velocity, the PSD shift to the coarse region and poly-dispersity in the other two regimes, the ligament in Figure 1.19.b) and sheet in Figure 1.19 c). Consequently, a higher rotational speed is needed to maintain powder quality and increase process yield. Rotary Electrode Process (REP) and Plasma Rotating Electrode Process (PREP) are typical for Titanium alloys powders production. By contrast, CA usually achieves a low production rate, such as less than 100 kg/min; otherwise, the quality of powders and the corresponding PSD are compromised. Moreover, a little introduction of O2 could strongly affect particle shape for specific alloys.

### 1.3.2.2 Water Atomization

Water Atomization (WA) is a two-fluid atomization technique in which highpressure water flux breaks metallic melt. The liquid film destruction forms particles. Powders are then collected in water and sieved or separated by a subsequent process. For this reason, there is no necessity for the passivation step (as will be explained in the following Chapter 2), and the process could be used continuously. It is assumed that the WA plant could reach a production rate of up to 500 kg/min. In terms of world production, WA is the most used technique for metal powder atomization. It is estimated that half of the world's iron powder production is manufactured by WA [61]. This is particularly true for copper alloys, pure iron, stainless steel, tool steel and magnetic powders for press and sintering processes.

High process yields could be obtained depending on the type of product required and the secondary liquid used. Indeed, changing secondary liquid could influence enormously quench effect. The water quench effect is one of the most drastic quenching secondary liquids. As a result, the solidification time is less than the spheroidization one (as explained in Chapter 2). Therefore, spherical powders are impossible to be produced. By contrast, using water as a quenching agent promotes oxide formation and impurities. The oxide issue could be solved using a different secondary liquid. Oil and hydrocarbons atomization has been developed since the 80s. In this way, very low O2 content powders can be produced. However, high melting point alloys (Tm > 800 ° C) trigger the pyrolysis process in oil. Due to the pyrolysis, the high C content is picked up by powders, so a decarburizing step is necessary. Moreover, the powder shape still maintains wrinkled and fragmented morphology.

Due to the reasons mentioned above, WA is not a recommended choice for LPBF production.

### 1.3.2.3 Gas Atomization

Gas Atomization (GA) is a two-fluid atomization technique in which high-pressure inert gas flux breaks metallic melt. Also, in this case, particles are formed by liquid film destruction. However, powders are directly collected in hoppers and do not need any separation processes. PSD of products could vary from  $< 10 \mu m$  up to mm. Consequently, several specific surfaces could be produced as a function of the needs.

Very high spherical particles are produced by GA techniques, except for satellite formation. However, the process introduces no oxide or contaminants into the powders. Moreover, a higher process yield could be reached by GA (150 kg/min) concerning CA. As a function of the LPBF machine, a minimum quantity of powders could be necessary for massive production. In addition, different kinds of inert gas can be used. The gas choice is fundamental for GA plant design (as explained in Chapter 2).

Finally, GA can be deemed an optimal choice for LPBF powder production. GA powder's characteristics fit all the main powder requirements for LPBF technology. Furthermore, GA is considered a Rapid Solidification Process (RSP) for its high cooling rate. Consequently, metastable phases can be produced, so new "impossible" alloys can be developed/designed.

## **1.4 GA and LPBF as Rapid Solidification Processes**

As already mentioned, GA and LPBF can be included within the RSPs techniques. Rapid solidification can obtain metastable phases. In addition, solid solubility limits can be exceeded [62]. Fine and homogeneous microstructures increase Yield Strength (YS), Ultimate Tensile Strength (UTS) and Elongation at break (A%) of almost any kind of alloy. Moreover, intermetallic precipitations can be produced with optimal morphologies, like spherical or globular instead of needle-shaped ones. For example, AlSi7Mg alloy can enhance its mechanical proprieties passing from cast to RSPed one, as can be observed in Figure 1.20.



Figure 1.20: Comparison between mechanical properties of AlSi7Mg produced by casting and RSP technologies; adaption from [64].

Many other material properties can be enhanced by RSPs (Young Modulus, coefficients of thermal expansion, hot strength). For this reason, GA and LPBF are promising processes for manufacturing new alloys.

## Chapter II

## **2** Gas Atomization

*Atomization* is a powder production technique based on the concept of breaking a liquid film. Historically, there is evidence of atomization techniques as early as the 15-16<sup>th</sup> century for producing precious metals in the shape of granulates. The need for granular products with consistent characteristics was in response to the demands of commercial activity and the exchange of goods and materials. In modern times, products with precise surface requirements have led to a gradual improvement of processes up to the present day. The evolution of industrial sectors (such as pharmaceutical, chemical, powder metallurgy and aerospace) has prompted considerable investments in powder production techniques.

As explained in Chapter 1, the choice of Gas-atomization (GA), among the other metal powder production techniques, responds to the stringent product characteristics necessary for Laser Powder-Bed Fusion (LPBF). Powders with spherical morphology, dense, ranging between 15 and 150  $\mu$ m, with homogeneous compositions and microstructures are obtained by GA. Each gas-atomizer consists of 4 main elements:

1. The melting chamber is where the fused metal liquid is obtained from raw materials by heating with electric resistance or by induction.

2. The atomization chamber is the area in which particle solidification takes place. Dimensions of the chamber depend on the type of atomizer (single fluid or two fluids), the type of secondary fluid used (such as gas, water or hydrocarbons) and the critical cooling system.

3. The nozzle is the connection area between the melting and atomization chamber. The melt flows through the nozzle, which crosses a flow of inert gas (such as Air, Nitrogen or Argon), which can disperse the metal film into particles upon being injected into the atomization chamber. The nozzle is the most delicate area of the system; even minor deviations from the ideal conditions could lead to a failure of the entire atomization process (also called run) or even atomizer breakdown.

4. Hopper and ancillary equipment are normally placed on the ground floor. The main collection hopper is where particles with a dimension of Diameter (D) >

15  $\mu$ m converge. Then, a separator cyclone divides particles with a size of D < 15  $\mu$ m into two streams. The first stream (with particles 1 < D < 15  $\mu$ m) ends up in the secondary collection hopper. These particles are collected at the end of the test campaign and disposed of as special waste. Due to their extremely fine particle size, they are generally not analyzed or mixed with the products obtained from the main hopper. The second stream (with particles at a dimension of D < 1  $\mu$ m) ends up in a gas filter placed above the separator cyclone.

In Figure 2.1, a 2-fluid GA plant with a close-coupled nozzle is illustrated.



Figure 2.1: Scheme of a two-fluid gas-atomizer plant; adaption from [65].

## 2.1 Melt and Atomization Chambers

### 2.1.1 Description of GA Plant in Alessandria

The GA system installed in Alessandria, as can be seen in Figure 2.2, occupies a volume of  $210 \text{ m}^3$  and spreads out across 3 floors.



Figure 2.2: Isometric view and dimensions of the GA plant.

The main control station of the system is placed on the second floor. All atomization phases could be controlled from the upper position, particularly the pre-atomization process. Loading the crucible, setting and controlling the vacuum inside both chambers, filling them with inert gas, ignition of the induction furnace, control of the crucible temperature, and the safety and metallization valves are all managed from the main control station. A screen can observe the evaluation of each process step near the main control station. The screen is connected to a camera focused on the nozzle. Therefore, the main control station operator manages the entire pre-atomization phase and can evaluate the progress of subsequent process steps.



Figure 2.3: Front view of Alessandria GA plant. Red dashes highlight melting chamber on the 2<sup>nd</sup> floor; Green dashes highlight atomization chamber on the 1<sup>st</sup> floor while yellow dashes highlight ancillary equipment and main collection hopper on the ground floor.

Figure 2.3 illustrates a front view of Politecnico's PSI Hermiga 100 GA plant. On the first floor is placed the secondary control station position. From there, metallization, atomization and post-atomization steps are managed. The metallization phase refers to the step of opening the valve at the bottom of the crucible. After the metallization step, melt metal flows inside the atomization chamber. At this point, the atomization button can be pressed to start the inert gas flow into the atomization chamber. After the finish of the atomization, the secondary control station managed the passivation step (for reactive powders). On the ground floor, ancillary equipment like hoppers (main and secondary), separator cyclone and gas filter are placed.



### 2.1.2 Description of GA Plant: Melt Chamber

Figure 2.4: Closed melting chamber ready for operation is showed.

In Figure 2.4, it could be seen in the outer part of the melting chamber. The top hat of the chamber is opened during the pre-atomization phase for two main reasons: the cleaning of the chamber and the loading of new material for subsequent atomization. The first phase can only take place after removing the powder products from the main hopper to cool down the system and bring it back to ambient pressure. This safety procedure also guarantees avoidance of an explosion when reactive powders are produced. The vacuum-inducted furnace is used to melt raw materials inside the crucible, which is bottom-poured. For these reasons, this type of plant is defined as a Vacuum-Induction Gas Atomizer (VIGA) with a bottom pouring crucible. In Figure 2.5, a scheme of the interior of the melting chamber is shown. A crucible (of alumina or, more rarely, graphite) is positioned inside the induction coil with the central axis corresponding to the guide tube assembly. The guide tube assembly is the parts in contact with the molten metal and the nozzle. Positioning the guide tube assembly above the nozzle is the first step of the process. Alumina fiber insulators are positioned around the crucible to insulate the guide tube assembly thermally. Two crucible gaskets (small squared alumina-fiber paper) are affixed to the top of the guide tube assembly in order to prevent molten metal spillage. The guide tube assembly is inserted inside the plug seal (located inside the crucible's bottom hole) to ensure metal flow inside the guide tube. The system's seal is guaranteed by alumina cement between the plug and crucible, although it must be hardened in an oven before usage. The crucible is coated with alumina-fibers insulating panels to avoid direct contact with the induction coil and ensure excellent mechanical stability.



Figure 2.5: Detailed scheme of the crucible placed into the melting chamber.

An alumina stopper rod is placed with guide tubes and plug seals to occlude the passage between the atomization chamber and the melting chamber. The occlusion of the guide tube is ensured by the mechanical conformation of the stopper rod, the plug seal and the guide tube surfaces. The conforming surfaces are prepared using diamond paste and imposing pressure on the stopper rod. This step guarantees the prevention of melt escape prior to the metallization phase. A loss of molten material before the metallization step will irreversibly occlude the guide tube, thereby preventing a successful run. The stopper rod is raised during metallization by the hydraulic actuator highlighted in Figure 2.4. Finally, the raw materials are placed inside the crucible assuring that the weight of the metal mass does not impact the stopper rod already in position.

### 2.1.3 Description of GA Plant: Atomization Chamber



Figure 2.6: Secondary control station at first floor of the GA plant in Alessandria.

The secondary control station is placed on the first floor (Figure 2.6). From this area, all the parameters relating to the atomization and the post-atomization phase can be controlled. As can be seen from Figure 2.6, the station is equipped with a porthole to observe the atomization trend. Safety glasses are necessary to avoid eye injury. The secondary control station indicates the real-time data of the system

(temperature and pressure inside both chambers) and features two process buttons: metallization (red arrow in Figure 2.6) and atomization (black arrow in Figure 2.6) buttons. The first is used to remove the stopper rod from its stationary position. At the same time, the atomization button initiates the injection of argon into the atomization chamber, thereby starting the production of powders. The splash-can is a crucible with a plugged bottom that is positioned under the nozzle before metallization. It is used to collect the first flow of non-atomized liquid metal to avoid its collection in the main hopper and contaminating the final products. Once the atomization step has been carried out, the splash-can is moved under a bulkhead inside the atomization chamber to prevent the particles from settling inside. It is important to remember that the atomization step must not start simultaneously as the metallization step. If the gas flow was cooled, the metal melted in the nozzle. This would lead to a failure of the run. Consequently, the two steps must be performed *consecutively* to evaluate a correct initial flow of material and, subsequently, to minimize the loss of materials in the splash-can.



Figure 2.7: Gas-control panel and O<sub>2</sub> sensor.

Finally, as shown in Figure 2.7, the gas-control panel is almost exclusively made up of manual valves and barometers, which must be adjusted according to the defined pressure. From this console, inert gas inlet pressures are adjusted for melting and atomization chambers (to guarantee a controlled atmosphere inside chambers during the process). The gas-control panel manages the pressure present at the nozzle during the atomization phase (atomization or die pressure). Finally, the powder's passivation phase could be controlled through the featured O2 sensor. The powder surfaces' passivation is necessary to avoid excessive heat formation and explosions. In fact, in the presence of O2, particularly reactive metals (like Al or Mg alloys), high and rapid heat formation could occur due to oxides reaction on powders surfaces as a result of exothermal processes [66,67]. Passivation takes place by modifying the atmosphere inside the system step by step. Between each step, it is necessary to wait an adequate amount of time for a complete particle surface oxidization, adapting to the present O2 concentration. This process is facilitated by moving the powders through a fluidizer gas sprayed directly into the hopper. The temperature inside the hopper is controlled during the passivation step by employing a thermocouple placed at its base. The whole plant (hoppers, melting chamber and atomization chamber) is built with a double vessel of AISI 304L. A cooling system is placed in the cavity to maintain a maximum temperature limit of 30 °C. The oxygen analyzer evaluates O2 concentration within the system. From material loading to the heating phase, the system used the vacuum to remove the gas from raw materials. Once almost half of the material's melting temperature is reached, the chamber is filled during the so-called "back-filling" step. Filling takes place with Argon, chosen as atomization gas. The melting chamber would be kept at a slightly higher pressure than the atomization chamber to facilitate the flow of the melt from one chamber to another and avoid melt-rising.

#### 2.1.3.1 Particles Solidification and Morphology

The dimensions of the melting and atomization chambers are by no means comparable (Figure 2.3). The melting chamber must be thermally responsive to bring the pre-atomized material to its melting temperature as quickly as possible. Likewise, the cooling process must be rapid after the atomization process is finished. Therefore, the most diminutive possible dimensions of the melting chamber are ideal. The atomization chamber confined gas and powders during solidification (and their subsequent collection). Therefore, particles produced must have a sufficient flight time to spheroidize and solidify.



Figure 2.8: Flight path length for complete solidification as a function of temperature and particle dimension; adaption from [63].

The time required for solidification is a function of the amount of mass present inside the particle and its volume. Solidification time is determined by two contributing variables: the time required to remove superheat and the time required to remove latent heat of solidification. In Figure 2.8, the distance required for a particle (of increasing diameter) to complete the solidification process is illustrated. As the space traveled increases, and therefore the exposure time, the temperature of the particle tends to equalize with the temperature of the gas. For a particle with a diameter of 18 microns, a flight space of less than 10 mm is required to achieve thermal equilibrium with the gas. However, if the size is twice (36  $\mu$ m), it is evident that at least 50 mm is necessary to obtain the solidification of the particle merely. As the size of the desired particle increases, it is, therefore, necessary to correctly design vessel dimensions to ensure adequate flight time (flight path length).

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Figure 2.9: Difference between solidification time and spheroidization time as a function of particle dimension for GA products [63]

On the other hand, a more detailed approach is required regarding particle morphology. For spherical particles, it is necessary that the spheroidization time, the time required for the particle to obtain the shape that minimizes the internal energy of the system (i.e. a sphere), must be greater than the solidification time. Fortunately, for inert gas atomized powders, spheroidization time is several orders of magnitude lower than solidification time (Figure 2.9). However, particle dimensions can modify the solidification process. Deviation from sphericity results from low superheat, which causes premature solidification. The presence of contaminants or surface oxide films can also have a role in increasing liquid viscosity. The satellites, by contrast, are caused by collisions between particles in flight. This event's incidence increases as powder size decrease since fine powder particles are drawn into the atomizing zone. Therefore, as can be seen in Figure 2.10, the presence of satellites strongly depends on the temperature at which the impact occurs with small particles in the atomization area caused by gas-recirculation.



Figure 2.10: Variation of morphologies as a function of particle temperature at impact [63]

Splat caps are formed if the impact between two particles occurs just below the liquidus temperature. Tiny hot droplets collapse above a larger one leading to cap formation. Since impact velocities increase the cooling rate, the cap could be characterized by nano-sized microstructure and precipitates. If the impact occurs between the liquidus and solidus temperature, the particles coalesce, leading to the formation of welded satellites or a deviation from sphericity. Impact under the solidus temperature can give rise to two distinct phenomena:

• For low impact energies (a large dimensional difference between the two particles), satellites can be formed via adhesion to the surface of the particle.

• If the particle size is similar (higher energies involved), rebound and expulsion of the satellite are observed, with deformation of the initial particle or breakage of the larger particle.

The presence of satellites in the powders produced by GA is therefore a function of the random impacts of smaller particles. In fact, the particles with reduced dimensions tend to remain in flight instead of bottom settling due to the recirculation motions of the gases inside the chamber. Figure 2.11 shows the distribution of the particles inside the chamber as a function of their size obtained through fluid-dynamic simulation.



Figure 2.11: Distribution of particles inside atomization chamber as a function of particle dimension; adaption from [68]

As can be seen in Figure 2.11, almost all of the particles between 75 and 135 microns fall and collect in the main hopper. The gravitational force on particles with this diameter prevails over other forces inside the vessel. The situation varies slightly between a dimensional range from 10 to 75  $\mu$ m due to an increasing percentage of particles suspended in flight. However, most particles still settle at the bottom of the vessel. Finally, a complete reversal of the trend is evident in the particle size class from 1 to 10  $\mu$ m. The force of gravity becomes negligible due to the small size of the particles. This fact ensures that the fine powder is distributed evenly within the vessel.



Figure 2.12: Distribution of particles inside atomization chamber as a function of particle dimension; a) modification of vessel height; b) modification of vessel width; adaption from [68]

As illustrated in Figure 2.12.a, an increase in the height or width of the vessel would not affect the dispersion of the finer components (Figure 2.12.b). Dimensional changes of the vessel cannot affect the presence of satellites as the recirculation of gases inside the chamber prevails over the other forces involved. In order to solve this problem, systems have been invented for injecting recirculation gas in ideal quantities to counterbalance the rising effects of the finest dust. When gas recirculation is not used, a substantial particle recirculation area arises near the atomizer. High particle concentration close to the nozzle leads to a high rate of collisions between larger semi-solid particles and small solid particles, resulting in non-spherical particles with satellites.

The sizing of an atomization chamber depends on the characteristics of the desired products (size and morphology) and the gases used in the plant. This last parameter will be detailed later as it strongly influences the dimensions and microstructures of the products by modifying the cooling rate. Pressure and temperature control within the vessel must be specific to the gas used.

## 2.2 Nozzle

The nozzle is the heart of every atomization plant. It is where liquid film formation occurs with its subsequent separation into particles. Given the fact that it undergoes high pressures and temperatures for the entire duration of the process, the nozzle is also the most vulnerable area of the system. The two main types of nozzles used in 2-fluid atomization are the free-fall nozzle (also known as the open nozzle) and the close-coupled nozzle (also known as the closed or confined nozzle). The free-fall nozzle was the first and simplest technology used for 2-fluid atomization. The melt descends by gravity inside a guide tube until it is disrupted at the gas flow convergence. The distance between the melt exit height and the gas-impact height varies between 5 and 10 cm to protect the nozzle from metal drops or splashes. This distance is needed to avoid freezing problems or flow interruptions and to maintain stable atomization conditions.

For this reason, a free-fall nozzle is preferable in systems that operate for several hours and produce large quantities of material. However, the distance between the melt exit point and the atomization zone affects the atomization efficiency. In fact, due to the lower kinetic energy of the falling melt, coarser products are obtained compared to the close-coupled ones. The cumulative mass distributions obtained by the two different nozzle types are shown in Figure 2.13.



Figure 2.13: Visual explanation of a) free-fall and b) close-coupled nozzles. Variation in nozzle design could strongly affect particle diameters; adaption from [69].

As can be noted from Figure 2.13, the curve obtained by atomization of CuSn10 alloy (bronze) with a close-coupled nozzle is much further moved to the left of the graph concerning the same powder produced with a free-fall nozzle indicating finer particle size fractions. With similar process parameters, particles with smaller average sizes are obtained thanks to the tremendous kinetic energy possessed by the melt at the moment of impact with the gas jet. On the other hand, the disadvantage of a close-coupled nozzle is the extreme cooling conditions that the gas-nozzle and the tip of the melt-nozzle undergo. Consequently, the area is subjected to high thermal stresses, which can cause the breakage or damage of the guide tube assembly and freeze the melt in the melt nozzle.



Figure 2.14: Detail of nozzle during atomization process; as a function of gas pressure, melt could reach gas-nozzle and freeze causing system breakage; adaption from [70]

As can be seen in Figure 2.14, there are areas of the nozzle in contact with both the fused metal (up to 1700  $^{\circ}$  C) and with the outgoing gas (down to -180  $^{\circ}$  C). These problems can be partially solved by using hot gases, which is the technique employed in the industrial production of aluminum powders. Temperature issue could be to worse by the velocity of inert gas and the nozzle design.



Figure 2.15: a) Gas jet apex angle ( $a^{\circ}$ ) and Melt tube tip angle ( $b^{\circ}$ ) are complementary angles which are related to nozzle design [64].

Another problem of the close-coupled nozzle is the conformation of the angle of attack of the gas-nozzle and melt-nozzle. Depending on these two angles, illustrated in Figure 2.15, the actual gas pressure can vary considerably. In the event of a very high angle between the gas flow and the melt flow, for example 90  $^{\circ}$ , benefits are observed on the cooling of the nozzle tip, but the back pressure is exerted on the metal melt which can lead to rising effects.



Figure 2.16: Variation of mass median diameter as function of gas velocity [71]. Gas jet apex angle and melt tube tip angle strongly influence gas velocity.

To avoid any issues, angles between 30  $^{\circ}$  and 60  $^{\circ}$  are industrially used, but this affects the outcome of the powders produced. In fact, when the angle between the gas jet and metal flow varies, there is a concomitant variation in the speed of the gas. In Figure 2.16, the trend of the average size of the powders is shown as a function of the gas velocity. At larger angles (60  $^{\circ}$ ), it is possible to obtain a higher gas velocity. Consequently, particles with a smaller average diameter are formed due to the greater kinetic energy available.

The angle of attack depends on the design of the gas-nozzle and the tip of the meltnozzle. It is therefore among the process variables that cannot be changed unless the design of the nozzle itself is modified. In industrial practice, the angle of attack is set with certain parameters by the plant manufacturer and is not modifiable.



### 2.2.1 Description of the GA Plant: Nozzle

Figure 2.17: Parts necessary for a complete guide tube assembly in a PSI Hermiga 100 plant type.

Figure 2.17 shows all the components necessary for the assembly of a complete melt-nozzle. The core of the melt-nozzle is composed of a boron nitride tip (1.a) joined to an alumina tube (1.b). To ensure the integrity of this joint as the temperature rises, the two components must be glued together with an alumina cement and kept in the oven at a temperature of 200 ° C until the beginning of the pre-atomization step. This procedure dually allows for the degassing of the material and the tight bonding of the two components. The graphite washer (1.c) is inserted just above the tip by passing it through the guide tube. Immediately above, two graphite springs (2) are positioned on the graphite washer, which will serve as heating elements for the guide tube. An alumina fiber insulator (3) is then placed on the outside to avoid overheating the external area of the guide tube assembly. The assembled semi-product is positioned inside the external structure of the guide tube assembly (4.a + 4.b + 4.c). All the pieces are made of Mo in order to maintain the necessary mechanical resistance at high temperature. The guide tube reaches a temperature of at least 200 ° C higher than the metal melting point to avoid a freezing effect inside the guide tube, resulting in a failed run. The two alumina washers (5.a and 5.b) are used to ensure electrical insulation between the two parts of the guide tube assembly (4.a and 4.c) in order to force a current passage through the graphite springs (2). The connection of the guide tube assembly is finally guaranteed by the Molybdenum connector (6), which is linked with the appropriate cable inside the melting chamber. Each of the steps listed is crucial for successful atomization. The tip (1.b) is drilled at a suitable size according to the process parameters. As will be detailed, the size of the hole at the tip of the melt-nozzle significantly influences the size of the atomization products.

### **2.3 GA Main Process Parameters**

The components of the atomization plant have been analyzed, indicating their role and impact on the overall process. However, it is essential to identify which GA process parameters exert the most significant influence on the final products. The previous sections presented the controls and criteria needed for a complete, correct run execution. Despite these checks, the results obtained often do not comply with desired results. Therefore, in order to control the characteristics of the final product, semi-empirical models have been developed over the years to establish correlations between the GA main process parameters and the final dimensions of the products since GA almost exclusively yields near-spherical particles.

# 2.3.1 Predictive models: Lubanska Model and Gas to Metal Ratio (GMR)

There is a large number of studies and analyses on the effects of GA main process parameters (superheat, gas pressure, mass flow rate, etc.) on the properties of powders. Initially, empirical models were developed on Water atomization (WA) and subsequently transferred to the GA plant. In one of the first studies conducted, Watkinson [72] realized that an increase in the average diameter of the final particles was obtained by decreasing the pressure of the atomization fluid (water) or increasing the flow rate of the melt.

Other variables were also taken into consideration, such as the angle of attack between the two fluids, the moment of water flow, etc., but none of these surpassed the degree of correlation between pressure and particle size. From this point, a law (1) was formulated by Small et al. [73]which allows operators that are using two-fluids atomization systems to calculate the relationship between the pressure of the atomization fluid and the size of the particles.
$$d_m = \ln \left(\frac{P}{A}\right)^n \tag{1}$$

In which  $d_m$  represents the diameter of 50% of the particles (average diameter); A and n are constants so that the  $d_m$  decreases with increasing P. P is the atomization fluid pressure. Clearly, other factors are related to this law such as superheat strongly influences  $d_m$ . In [73] the correlation between  $d_m$  and gas pressure (argon) was also noted using the same formula (1) developed for WA in a GA plant in the production of Co based alloy powders. However, die pressure does not affect the shape of the curve of the Particle Size Distribution (PSD). Rao [74,75] obtained similar results on Fe-based alloy powders using nitrogen as an atomizing gas. Moreover, Klar e Shafer [76] also confirmed this trend for Cu-based alloys.

Another important parameter for controlling particle size is the Ratio of Gas flow to Metal flow (GMR). Starting from the work carried out for WA, Lubanska [77] in 1970, formulated a semi-empirical relationship to evaluate the variation of particle sizes as the GMR varies. This study was based on the results obtained from the atomization of Fe, Al, Cu and Sn-based alloys and therefore included variables relating to both the type of plant and the material produced.



Figure 2.18: a) The Lubanska equation and its alignment with experimental data; adaption from [77]. b) influence of GMR on cumulative weight fraction; adaption from [64]

In Figure 2.18.a) it is possible to note how the points obtained from the experimental results are in agreement with the equation developed by Lubanska, which is highlighted in Figure 2.18.a). Regarding the variables used:  $d_m$  represents the diameter of 50% of the particles (average diameter);  $\delta$  is the hole size of the meltnozzle (µm) shown in Figure 2.17,(1.a);  $V_m$  is the kinematic viscosity of the fused metal (m<sup>2</sup>/s);  $V_g$  is the kinematic viscosity of the gas (m<sup>2</sup>/s);  $W_e$  is the Weber number of the atomization gas; M is the mass flow rate of the molten metal (Kg / s); A is the mass flow rate of the atomization gas (Kg / s); K is a constant. Therefore, GA influential variables could be attributed to the type of plant ( $\delta$ ,  $V_g$ ,  $W_e$ , A) or to the type of material used ( $V_m$ , M). Using the cumulative curves obtained from Mass PSD, it is possible to note (in Figure 2.18.b) the shift to larger particle sizes as the GMR decreases. For the above reasons, following parameters could be used to modify the average size of the particles and manage the GA products production.

### 2.3.2 Melt-nozzle hole size

The size of the hole in the melt-nozzle ( $\delta$ ) directly influences the size of the particles by modifying the fluid-dynamic conditions in the formation of metal film from which the particles originate; the increase in the size of the hole is therefore directly proportional to the increase in  $d_m$ . This parameter is identified before the loading phase of the melting chamber and modified starting from the minimum recommended diameter (1.5 mm).

### 2.3.3 Melt temperature

The melt temperature and superheat ( $\Delta T$ ) decrease the  $V_m$  of the metal melt and consequently increase the mass flow rate M; this means that an increase in temperature will lead to an increase in  $d_m$ . In addition, two important aspects should be remembered prior to changing previous parameters: first, the increase in the temperature of the melt can lead to boiling of the metal in the crucible. This effect would not only risk damaging the system, but also cause the low-melting elements to evaporate very quickly. This second effect would alter the quality of the final product, depleting it of necessary elements, as well as the performance of the system by modifying the  $V_m$  with undesirable effects on the  $d_m$ . For this reason, manufacturers always recommend operating within a maximum range between 200-250 ° C of superheat. However, it is suggested to not exceed 1700 ° C, which is the upper limit of the system.

### 2.3.4 Chemical composition

Chemical composition modifies the  $V_m$  of the metal melt and consequently modifies the mass flow rate M; this parameter is evaluated when the formulations of the alloys available on the market are modified in order to adapt the other parameters accordingly. The change in composition affects both the  $d_m$  and the microstructure of the products.



Figure 2.19: Influence of chemical composition and cooling rate on cell spacing [78]

An example is shown in Figure 2.19, in which it is possible to note the variation of the Cell-Spacing as a function of the cooling rate as the composition changes. As the % of Cu present in an Al-Cu alloy increases with steady Cell-Spacing (2  $\mu$ m), higher cooling rates are needed due to the different compositions (500, 3500, 4800 K/s). It follows that the chemical composition is not a useful parameter for controlling the size of the atomization products.

### 2.3.5 Gas type and gas temperature

Temperature and type of gas can modify the parameters relating to the atomization gas  $(V_g, W_e, A)$ . Increasing the gas temperature has the advantage of significantly reducing median particle sizes in powders due to the increased kinetic energy imparted on the gas stream, as illustrated in Figure 2.20.



Figure 2.20: Influence of gas temperature on  $d_m$  for Pure Ag (Ag), Stainless Steel (SS) and Pure Au (18K) [79]

The effect is shown for different types of material (Pure Ag, Stainless Steel, Pure Au) in order to demonstrate the effect of the  $V_m$  of the melt. Unfortunately, the use of this type of technology requires a special section of the plant to be dedicated to the recirculation and heating of gas. As for the type of gas, using gas with higher thermal conductivity and lower density can influence the heat exchange with the particles and consequently the cooling rate. In Figure 2.21.a) the effect of the gas variation on the cooling rate as a function of the particle size can be seen. Helium has a conductivity almost 7 times higher than that of Nitrogen and a density 8 times lower. This also implies being able to obtain finer particles, as shown in Figure 2.21.b), with the same process parameters.



Figure 2.21 a) Cooling rate variation as a function of the type of gas used [78]; b) influence of gas type on cumulative particle size distribution [80]

However, the choice of the type of gas must also be made according to the admissible costs to produce the powder: using He costs 200 to 300 times more than using  $N_2$  and 20 to 30 times more compared to Ar. Furthermore, the use of He can only take place if the system has been specifically designed to use it (gaskets, connections, pipes, etc.). Therefore, the use of  $N_2$  seems to be the best choice from this point of view; however, it must be noted that  $N_2$  is reactive with most of the metals and therefore cannot be used for all of them. For example, it is an optimal gas for the production of Cu powder as  $N_2$  is totally immiscible in the metal.

### 2.3.6 Top Pressure

Top Pressure is the difference in pressure between the melting and atomization chambers. It modifies the quantity of metallic flow per unit of time i.e. M, mass flow rate. A minimum Top Pressure value is necessary to ensure the descent of the melt through the nozzle since using a close-coupled nozzle presents a strong risk of freezing. This is accentuated as the atomization pressure (die pressure) increases and the angle of attack increases for reasons explained in the "Nozzle" paragraph. Therefore, as the Top pressure increases a larger particle size should be obtained but this is not entirely true. In more recent studies [81,82], the limited influence of GMR on the particle size was noted in plants with close-coupled nozzles. In fact, it

is stated that, although the GMR is an excellent predictor of the standard deviation, it does not have a marked influence on the  $d_m$ . The dominant parameter for control of the mean droplet diameter, termed  $d_m$ , is the mismatch in velocity values between the gas and the melt,  $\Delta U = U_g - U_m$ , defined at the location of contact with the high velocity gas (at the outer edge of the melt pour tube tip) during primary break-up [83]. Despite this, in the industrial field, GMR is still used as a parameter for evaluating the performance of the plant. Furthermore, the Top Pressure can be set within a very narrow range of values. Below 0.2 barg, there is a risk of incorrect melt leakage. Barg (from "bar gauge") represents the difference between the pressure in bar in a space and the atmospheric pressure in bar. Above 0.5 barg, bursting disks break and graphite windows rupture in order to not exceed the pressure limit inside the system.

### 2.3.7 Die Pressure

Die pressure or Atomization Pressure is the parameter that most directly influences the GMR. Increasing the die pressure directly modifies the speed of the gas during its impact with the metal flow and therefore decreases its  $d_m$ . However, depending on the type of metal to be evaluated, it is necessary to maintain an adequate working range to avoid the following problems. Specifically, an excessive decrease in die pressure can lead to extremely coarse particles (> 200 µm), which are not suitable for processing in LPBF. Furthermore, with the further decrease in the speed of the gas, it is possible that the metal melt film does not disperse into particles, leading to a high percentage of flakes unsuitable for processing by AM. The extreme increase in die pressure can instead lead to a rise in the metal flow due to the speed of the gas at the melt-nozzle. In this case, the phenomenon of freezing takes place. That is, the cooling of the melt inside the guide tube and the subsequent interruption of atomization. The variation of the die pressure was therefore chosen as the first parameter to be analyzed in the production process of metal powders. \_\_\_\_\_

## **Chapter III**

## **3 Validation of Gas-Atomization IAM Plant**

# 3.1 Production by Gas-Atomization of AISI 304L powders: State-of-Art

In August 2019, a PSI Hermiga 100 Gas Atomizer (GA) Plant was installed at Politecnico di Torino (Alessandria site). A first experimental campaign on AISI 304L was started to assess the repeatability and reliability of the plant. Powders obtained were characterized to compare their properties with commercially available ones. First, the effects of a variation of the GA process parameters were evaluated. Then, the feasibility of processing the powder was assessed for Additive Manufacturing (AM) technologies, and in particular, using Laser Powder Bed Fusion (LPBF) technique. LPBF process parameters were selected for a Concept Laser Mlab Cusing R machine to obtain whole dense samples. A comparison between the different optimized process parameters and several production technologies was carried out.



Figure 3.1: Powder Supplier Evolution and the Most Profitable Materials in the Worldwide Market [4].

According to Woheler Reports [4], the amount of metal powder retailers in the world is steadily growing compared to all major metal alloys, as illustrated in Figure 3.1.a. Among all alloys, steels are by far the most produced and available materials on the market. From Figure 3.1.b, it is possible to note which are the most profitable materials in the AM field in the year 2020. 75% of all material is solely attributed to the sum of Aluminum alloys (mainly AlSi10Mg), Titanium alloys (mainly Ti-6Al-4V) and Steel (mainly 316L). The availability of other types of alloys remains a niche sector.



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Figure 3.2:a) Market distribution of AM supplier/service/producer during 2020 [4]; b) Scopus quantification of papers during last 10 years; keyword used TITLE-ABS-KEY ( 304L) AND TITLE-ABS-KEY (ADDITIVE / TITLE-ABS-KEY ( 316L) AND TITLE-ABS-KEY (ADDITIVE )[49].

Although AM of metallic materials is still partially relegated to the academic institutions (15% of the global market), utilization of AM in the aerospace and automotive sectors are increasingly gaining importance (Figure 3.2.a). An example was the decision of the F1 Alfa Romeo team to increase AM manufactured car parts by 113% from the previous year, of which 22% was made in AISI 304L [84]. As evident in Figure 3.2.b, from 2012 (the year in which the first study on process feasibility of 304L through AM was published) to 2018 (the starting year for this research), publications in the AM field for AISI 304L did not exceed ten per year compared to the much more ubiquitous 316L material. During the last few years, however, the scientific community has investigated the production and characterization of AISI 304L through AM.

304L is the most produced and studied austenitic stainless steel in traditional engineering fields [85]. This type of steel is a Fe-Cr-Ni alloy with Cr contents varying from 18 to 20% and a Ni content varying between 8 and 12%. Type 304 is the most popular grade of the 300 steel series. It is used for a wide variety of applications which require a good combination of corrosion resistance and formability [86]. The presence of C higher than 0.03% makes this steel extremely sensitive to the intergranular corrosion phenomena. The use of the L-variant (i.e.

Low Carbon content) is needed to prevent the precipitation of Cr carbides and the consequent embrittlement of the material.

GA powder production is a critical sector in scientific literature. The lack of sources over the last 30 years is mainly due to the high cost of purchasing and operating a GA plant as well as the lack of interest from industry. Some monographs and books have been reference points in the study of atomization process [61,63]. Lawley [61] firstly summarized the necessities of powder metallurgy industry. Through his monograph, most of the studies developed between '70 and 90' have been transmitted to younger generation. The tome develops mainly on the different technologies of powder production by atomization (water, gas, oil) with some hints on powder characterization and on physical models and mechanisms of atomization. Some years later, Dunkley and Yule [63] expanded Lawley's work providing a further more detailed tome on atomization. They work on atomization plant both from end-users and from designer point of view. Hence, a Computational Fluid-Dynamic (CFD) approach was used to define many atomization process parameters. In the end, an economic evaluation of the production chain was developed in order to enhance plant productivity.

For many years, the interest of the scientific community contracted. However, thanks to the explosion of AM technologies, this trend is recently reversing. Kalinin et al. [87] developed a KhN60M powder alloy (wt %: Ni bal., 14.0-16.0 Cr, 14.0-16.0 Mo, ≤4.0 Fe, ≤0.08 C, 1.0–2.0 Mn, ≤0.50 Si, ≤0.015 S, and ≤0.015 P) by GA using a VIGA 2B laboratory installation (ALD, Germany). Argon was used during the atomization process. They analyzed how atomization pressure influences powder properties and the atomizing process yield for 40-80 µm size class. Moving from 22 to 25 bar as atomizing pressure, a bigger fraction of powder was highly spherical classified (AR > 0.90). Therefore, better flow properties were detected. On the other hand, the yield of the target fraction (40-80  $\mu$ m) decreased from 30 to 22%. Qi et al. [88] evaluated the sphericity and the microstructure of a GA martensitic stainless steel (FeCrNiBSiNb) produced by Nitrogen GA. The N<sub>2</sub> choice influences the microstructure of powders because modified austenite final content. N<sub>2</sub> is an highly soluble gas in Stainless Steel and acts promoting austenite formation. Moreover, the dimensions of powders could also affect solidification path. Bigger particle dimension is correlated to a slower cooling rate. For this reason, transformation of austenite is incomplete during subsequent martensitic transformation and some austenite is retained. Nevertheless, homogeneous elements distributions are provided inside each particle. Atomization yield was measured as 35%. Salandre et al. [89] investigated the development of a new steel

composition named L40. Chemical composition of L40 is close to EOS MS1 Maraging Steel L40 powders were both gas-atomized and water-atomized in order to compare powder characteristics from the different production processes. GA powders were produced with Atomising Systems Ltd (UK) Gas-Atomizer using Nitrogen as atomization gas. Water atomized (WA) powders were commercially provided by Formetrix company. Then, GA and WA powders were processed by a 400 W EOSM290 to evaluate the mechanical properties of artifacts. SST approach was used to define a small process parameter window. GA samples reached more than 99.9 % of relative density while WA samples do not exceed 98.9 %. This is due to an inhomogeneous powder distribution caused by a lower aspect ratio of WA powders respect to GA ones. Both WA and GA-L40 samples showed better Yield Strength (YS) and Ultimate Tensile Strength (UTS) respect MS1 produced by the same machine. However, WA samples were affected by a 1% of porosity which reduced Toughness in both XY and Z-directions. Metal-Matrix Composites (MMCs) could also be produced by GA. Perminov et al. [90] developed a Fe-TiC composite by an atomization unit VIGA 1B (ALD Vacuum Technologies GmbH). Starting from a Ti-C rich Fe melt (1 wt% C and 4 wt% Ti), they took advantage of the TiC precipitation during the atomization phase to obtain Fe matrix enriched by in-situ formed µm-TiC. Increasing atomizing temperature, finest powder size distribution was produced. Nevertheless, the influence of atomizing temperature during the process shall be investigated in future works.

Yodoshi et al. [91] focused their works on powders porosity. They produced an  $Fe_{76}Si_9B_{10}P_5$  amorphous alloy (atomic%) by a gas atomization (RQM-P-100, Makabe Giken Ltd., Sendai, Japan). Pores presences were correlated with 2 atomizing parameters: atomization pressure and atomizing gas type. Synchrotron X-ray CT was used for pores detection inside particles. With the aforementioned techniques, 0.65  $\mu$ m<sup>2</sup>/pixel accuracy could be reach. Consequently, particles smaller than 6.5  $\mu$ m were excluded by the analyses. The study demonstrated that low atomizing pressure (relative to the atomize material and the other process parameter) could positively affect pores content in powders produced. On the other hand, PSD shifts to coarse region. By the way, the utilization of reducing atomizing gas (such as H<sub>2</sub> or Ar + H<sub>2</sub> mix) could also prevent the formation of porosity. Smaller quantities of pores are obtained by the reduction of the thin oxide layer around the particles. Oxide layers are more viscous than metal melt. Therefore, pores coalescence and expulsion from the particles is prevented. Deirmina et al. [92] investigated the effect of 2 different type of GA on final properties of 18Ni300

LPBF samples. A first batch on powder was produced by a Vacuum Induction melting, and inert Gas (Ar) Atomization (VIGA), while the second batch was manufactured using inert gas atomization (IGA). Cubic samples were produced by a 400 W EOS M290 equipped with Yb-fiber laser. The utilization of Vacuum assisted induction melting decreased the total volume of O<sub>2</sub> and N<sub>2</sub> content from 320 to 170 ppm and from 240 to 45 ppm, respectively. UTS, YS and Elongation at break % (A%) values were constant. However, a decrease in Toughness and Fatigue Strength were detected. A reduced Fatigue Strength and toughness values could be associated to an increased presence of O/N-precipitates which act as stress intensification sites. Same trend was already demonstrated between GA and WA powders [89].

Previous authors focus on characterizing the powder produced by GA. Whereas, none of them investigated atomization process in detail. Li et al. [93], for example, analyzed the effect of nozzle diameter variation on powder characteristics. The yield of the process was calculated as the quantity of LPBF powders were produced (15-53 µm) respect to the total amount of products. As nozzle diameter increases, process yield and oxygen % content decreases. Both results could be associated to a coarsening of the mean particle diameter. As the particles get larger, the smaller the number of particles in the 15-53 µm range becomes. At the same time, specific surface decreases and, consequently, oxygen absorption. This trend was also confirmed by Kaiji et al.[94] which studied the effect of atomization pressure on hollow particles formation. The work confirmed the inverse correlation between atomization pressure and hollow particle % quantity. Reduce the atomization pressure and the turbulence of the gas flow reduce the chance of hollow powder production. On the other hand, lower atomization pressure produces coarser powders. Finally, Urionabarrenetxea et al. [95] deeply investigated the influence of all main atomization process parameters using a PSI Hermiga 75. 66 Atomization was performed to understand the following variables in the process: chemical composition, atomization gas type, top pressure, atomization temperature and atomization pressure. Gas-to-Metal Ratio (GMR) is the ratio of mass flow rate parameter calculated as gas mass flow used during atomization divided by metal flow rate. All atomization parameters influence mass GMR, and it is used to correlate process parameters to produced particle dimensions. Mass GMR was detected as an unreliable parameter to predict product size even if it is a widespread parameter. On the other hand, volumetric GMR seems to be a reliable alternative for process-products correlation. The atomization pressure is founded as the most relevant atomization process parameter.

Notwithstanding a recent growth in atomization scientific literature, no previous research analyzes the AISI 304L transformation process starting from raw materials to AM powders. The goal of the present chapter is to fill this knowledge gap. The plant parameters were studied to compare products developed in-situ with commercial ones. Therefore, this opportunity was used to validate an internal powder production system. First, the homemade powders were characterized as a function of the GA parameters. For this reason, physical (Particle Size Distribution, He-Pycnometry, Morphological measurement), chemical (Infrared absorption on combustion gases, Energy Dispersive X-ray, X-Ray Diffraction) and rheological analyses (Apparent, Packing and Tap density, Funnel Test, Angle of Repose, Hausner Ratio and Compressibility Index) were carried out. The results were compared with values present in scientific literature and with commercial products.

## 3.1.1 Gas-Atomization process parameters evaluation for AISI 304L

Atomization Pressure (or die pressure) is the parameter that most directly influences the Gas- to-Metal Ratio (GMR), as explained in "Chapter 2". Increasing the die pressure directly modifies the speed of the gas during the impact with the metal flow and therefore decreases the mean particles dimension  $(d_m)$ . Modification of die pressure in the first experimental trial was decided upon for the abovementioned reasons. Atomization Temperature, Nozzle diameter and Top Pressure (the difference between Atomization chamber pressure and Melting Chamber pressure) were maintained constant. Round bars of AISI 304L were provided in the form of 25 x 100 mm (L'inossidabile S.R.L., Torino, Italy). Chemical composition could vary within a standard range [96]. Quantometer analyses were used to check chemical composition. Results are reported in Table 1:

	ASTM A240	This Work
Fe	Bal.	Bal.
Cr	18.0-20.0	18.0
Ni	8.0-12.0	8.0
С	0.03	0.02
Mn	2.00	1.50
Р	0.045	0.03
S	0.03	0.03
Si	0.75	0.41

Table 1: Chemical composition of AISI 304L as defined by ASTM A240 [96] and one measured by at least 3 repetition by Qauntometer test.

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Ν	0.10	0.08

To validate the GA plant, 5 runs were carried out with AISI 304L as material. Each production test, from raw materials preparation to powders production, was named Run. 3 different die pressure were selected: 35 bar was chosen as suggested by plant producers; 40 and 45 bar were selected to improve the mass yield of powders products in 20-53  $\mu$ m range. 20-53  $\mu$ m range was selected as function of the final forming technology (LPBF). 35 and 40 bars pressure tests were carried out twice for the evaluation of process repeatability. The 45 bar condition was tested only once as it was considered the technological limit of the GA plant assuming the aforementioned working conditions. Process parameters were chosen as followed in Table 2:

Table 2: GA process parameters adopted for AISI 304L processed by PSI Hermiga 100.Investigation was focused on the influence of die pressure variation

RUN	Die Pressure (Bar)	Atomization Temperature (° C)	Top Pressure (Bar g)	Nozzle Diameter (mm)
1a*	35			
2a	40			
1b	35	1600	0.25	2.5
2b	40			
3	45			

As descripted in "Chapter 2", GA divides collected powders in two different hoppers as function of their size. In order to analyze the whole batch produced by the GA, in run 1a, particles in principal and secondary collection hoppers were mixed together. For this reason, it was chosen to named it <u> $Ia^*$ </u>. In the other runs, the fraction collected in the secondary hopper was excluded from the analyses due to its extremely fine dimensions (for both health and processability issues).

To assess GA performance, yield process was initially evaluated through a mass balance between raw materials and products. Round bars were loaded in a total amount of 5 Kg for each run. 500g was set as minimum quantity of powders for a complete characterization. For this reason, 5 Kg limit was set as a proper compromise between the minimum quantity of powder and the maximum load capacity of the crucible. To avoid any variation on metallostatic pressure during the atomization phase, the weight was kept constant. In Table 3 the atomization yields, obtained by sieving techniques, are noted:

Run	Initial Weight (g)	Principal Hopper Fraction (g)	Secondary Hopper Fraction (g)	20-53 μm Fraction (g)	20-53 μm Fraction Yield (%)
1a*		4337	224	1076	20
2a	5000	4500	235	2303	47
1b		2971	340	1525	31
2b		4584	240	657	14
3		3629	261	1920	39

Table 3: Atomization mass yield measured after sieving. 20-53 $\mu$ m class range is selected as function of the final forming technology (LPBF)

Red marked values in Principal Hopper fraction were lower, respect to black ones, due to technical problems. In run 3, with only 66% of yield obtained, the atomization (the opening of Die-gas pressure valve) was started late compared to the opening of the metallization valve (the valve which controls metal melt flowing). Consequently, a greater fraction of metal melt had settled inside the splash-can compared to other runs. On the other hand, during there was a rise of metal melt from the nozzle due to the high die pressure.

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Figure 3.3: Solid block caused by melt rising. The cooling of the melt in the guide tube formed a solid cylinder in the duct. This event did not allow the end of atomization.

The atomization continued until the sum of the Top Pressure and the metallostatic pressure of the melt were able to counteract the die pressure that caused the liquid to rise. Argon and melt rising did not allow for the completion of the run due to the formation of a solid block at the bottom of the crucible as shown in Figure 3.3.



Figure 3.4: Variation of  $D_{v50}$  as function of Atomization pressure. Values are compared to literature [95] produced by similar plant (Hermiga 75 instead of Hermiga 100) and similar composition (316L instead of 304L). While gas type could be differed, same process parameters were used.

The influence of atomization pressure on the Dimension of 50% (D<sub>v50</sub>) of particles measured by Volumetric Particle Size Distribution (PSD) is showed in Figure 3.4. As the pressure increases, the  $D_{v50}$  decreases as descripted by literature.  $D_{v50}$  values were measured by laser granulometer as described in "Analytical methods" Chapter. 1a\*, 1b, 2a and 3 atomization process parameters follow the same trend of a 316L powder processed by similar GA plant and condition [95]. Notwithstanding, 2b condition is out of trend probably due to an unexpected change in production parameters. Gas contribution seems to be ineffective on particle dimension variation. Hence, N<sub>2</sub> is sometimes used for Stainless Steel powders production. For example, Boes [97] produced X30CrMoN15-1 martensitic steel powders by N<sub>2</sub> atomization. Spherical and dense powders were obtained but with a N<sub>2</sub> highcontent. During LPBF, N<sub>2</sub> is lost but a significant amount stays in the additively manufactured part. N<sub>2</sub> presence improves secondary hardenability due to austenite transformation and carbide formation. However, brittle behavior is promoted and fatigue strength drop appeared. For this reason, Ar was chosen as atomization gas even if it is high-cost alternative.

Whereas the technical issues, 20-53  $\mu$ m fraction yield was considered consistently with literature values [87,88]. Values between 20-40 % as yield are considered acceptable from scientific community. 2b 20-53  $\mu$ m fraction yield is lower than 2a values but also respect to 1b values. However, 500 g of powders were still produced. It is considered enough for a complete characterization and acceptable value for our purpose.

### 3.1.2 Gas-Atomized AISI 304L powders characterization

3.1.2.1 Particle Size Distribution Analyses

Once powder production and process yield were assessed, powders characterization must have been done. Each run was separately characterized by physical, chemical and rheological analyses. Atomization yield in 20-53  $\mu$ m size range was firstly evaluated by sieving. Mass PSD was calculated by sieving technique as reported in "analytical method" chapter. In Figure 3.5 are shown Mass PSD for produced runs:



Figure 3.5: Mass particle size distribution of AISI 304L powders produced by PSI Hermiga 100. Size class were selected as function of possible forming technology (Metal Injection Molding or MIM, Laser Powder Bed Fusion or LPBF, Electron Beam Melting or EBM and Direct Energy Deposition or DED).

In Figure 3.5, D is considered the particle diameter. For PSD measurement, assumption of perfect sphericity was done. Each size class was associated to a specific forming technologies. As already mentioned, 20-53  $\mu$ m size class was selected for our purpose.

Run-1a\* owns 20% of its relative mass in 20-53 & D >106 µm size classes. The highest amount of powders falls in 53-106 µm. A little amount of powders seems to belong to  $< 20 \ \mu m$  size class even if secondary hopper powders were added. Hence, run 1a\* parameters optimize powder production in DED/EBM size classes. Therefore, as already discussed in "Chapter 2", higher die pressure was selected to increase LPBF powders production. Run-2a was performed at 40 bar (5 bar more than run-1a\*). A pronounced finer-dimension shift of Mass PSD was detected. A reduction of 53-106 µm and an increase of 20-53 µm size classes were obtained. By contrast,  $D > 106 \mu m$  size class remained constant while  $D < 20 \mu m$  increases up to 10 %. Consequently, a further increasing in die pressure was adopted. Run-3 was performed at 45 bar. An equal mass frequency was obtained by LPBF and DED size classes. Even though, run-3 was not completed for an Ar rising in the guide tube during the atomization. For this reason, die pressure was not increased anymore nor run-3 was tested again. Runs 1b and 2b were performed to confirm yield mass production. Neither 1b nor 2b confirm result from first trials. However, the lack of particles in the  $D < 20 \ \mu m$  size class for 1a\* and 2b runs is suspicious. This is especially true for run-1a\* in which a discrete amount was predicted. Moreover, both runs have the higher amount of particles in 53-106 &  $D > 106 \mu m$ . These clues could indicate the presence of agglomerates formation of very fine particles. Consequently, agglomerates are trapped in coarser sieves and classified as particles of higher dimensions. Volumetric PSD are then studied to avoid artifacts consideration.



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Figure 3.6: Volumetric particle size distribution of AISI 304L powders produced by PSI Hermiga 100. Size class were selected as function of possible forming technology. Volumetric analyses were due to avoid agglomerates artifactions.

In Figure 3.6, Volumetric PSDs of AISI 304L home-made GA powders are illustrated. As descripted in "analytical methods" chapter, Volumetric PSD is purged by artifacts contamination by its technical procedure. Indeed, run 1a\* enhanced its  $D < 20 \ \mu m$  particles content comparable to other runs. As consequence, LPBF and DED powders concentration seems to converge to other runs similar values. By contrast, run 2b maintain a low  $D < 20 \ \& 20-53 \ \mu m$  concentrations, while a very high amount of particles in  $D > 106 \ \mu m$  size class was recorded. This could be attributed to misleading die pressure value detection. In addition, by Volumetric PSD, the effect of die pressure variation seems to vanish. Trough Volumetric PSD is so not distinguishable the effect of die pressure variations.

artifacts and enhances each particles contributions, could be calculated. Numerical PSD avoids the distortion effects of volume contribution on PSD measuring, as detailed in "analytical methods" chapter. For this reason, numerical PSD was performed.



Figure 3.7: Numerical particle size distribution of AISI 304L powders produced by PSI Hermiga 100. Size class were selected as function of possible forming technology. Numerical analyses were due to avoid volumetric artifactions.

In Figure 3.7, Numerical PSDs of each run are noted. As could be immediately seen, more than 90 % of particles falls in D < 20  $\mu$ m size class. Y-axes break is used to enhance the difference between runs. As could be seen, 1a\* and 1b runs showed repeatable values. Same trend is illustrated for 2a and 2b runs. Run-3 owns the higher amount of D < 20  $\mu$ m particles as predicted by literature [61,63]. Fine powder amount is directly correlated to die pressure variation with an acceptable

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repeatability. Despite in run 1a\* principal and secondary hopper particles are mixed, it remains the run with the lowest number fraction in D < 20  $\mu$ m class. This can be attributed to the inability of the image analysis method to detect and evaluate spheres with a D < 1  $\mu$ m (image analyses algorithm lists them as a measurement error). Dividing the size classes even further and focusing on 75-106 & D > 106  $\mu$ m, a suspicious trend was retrieved.



Figure 3.8: a) Comparison between mass and volume PSD in  $75 < D < 106 \mu m$  size class; b) Comparison between mass and volume PSD in D > 106  $\mu m$  size class.

As can be seen in Figure 3.8.a, up to the fraction  $75 < D < 106 \mu m$ , mass and volume distributions do not coincide. Higher fraction detected by mass PSD are associated to agglomeration phenomenon. Frequency is evaluated in %, in such a way to be able to compare the curves obtained with different measurement methods. However, in D > 106  $\mu m$  size class (Figure 3.8.b) there is inversion between volume PSD and mass PSD. In these cases, a variation in the local density of the particles could be related to a great amount of hollow particles. Powder relative densities measurement were then performed.

### 3.1.2.2 Relative Density Analyses

Powders density was evaluated using 2 different techniques: He-Pycnometry and Image analyses of powders cross-section. Both techniques are discussed in detail in "Analytical Methods" Chapter. The presence of pores inside the particles was confirmed by the OM/SEM Image analyses of powder cross-section as shown in Figure 3.9.



Figure 3.9:As example, size class  $32 > D > 53 \mu m$ ,  $63 > D > 75 \mu m$  and  $D > 106 \mu m$  are shown. Pores are present in every size class. By contrast,  $D > 106 \mu m$  seems to own the highest % of particles voids.

As can be seen from Figure 3.9, pores are evident in almost all size classes. As example,  $32 > D > 45 \mu m$ ,  $63 > D > 75 \mu m$  and  $D > 106 \mu m$  size classes were reported. However, the % of voids differs for each size class. For run-1a\*, a complete cross-sectional Image analyses were carried out. Results are reported in Table 4.

Size class	Total Analyzed Area (pixel)	Total Pores Area (pixel)	%
		(r · · )	
D < 20 μm	267146	114.32	0.0
20 μm > D > 32 μm	194807.6	51.43	0.0
32 μm > D > 45 μm	198214.7	1276.88	0.6
45 μm > D > 53 μm	124294.4	59.50	0.0
53 μm > D > 63 μm	102768.3	145.24	0.1
63 μm > D > 75 μm	1157226	5574.36	0.5

Table 4: Run-1a\* cross-section Image Analyses results. Images of powders from D > 20 µm are obtained by OM. For a better resolution, D < 20 µm images were taken by SEM.

75 μm > D > 106 μm	1652360	1349.16	0.1
D > 106 μm	10582244	249990.58	2.4
		ТОТ	3.8

**Production** by Gas-Atomization of AISI 304L powders: State-of- 3—73 Art

Results show a low presence or absence of pores in  $D < 32 \ \mu\text{m}$ . From  $32 > D > 106 \ \mu\text{m}$ , a slight presence of empty particles is up to 0.6 %. D > 106 \ mm is definitely the size class with the greatest presence of pores with a 2.4 %. Porous powders are frequently produced by the so-called "Bag-crushing" mechanism illustrated in Figure 3.10.



Figure 3.10: Bag-crushing mechanism for hollow spheres formation. If viscosity is too high, secondary droplet formation is suppressed [63].

As predicted by the literature [94], the higher the kinetic energy, the greater the amount of porosity. If the viscosity rises sufficiently, the sheet collapses on itself to form a large drop (hollow sphere) with a trapped pocket of atomization gas inside (Figure 3.10) [63]. This is especially true for unsoluble gas in powders metal (Ar for example). Moreover, the presence of reducing gas is now used as strategy for hollow spheres reduction [91]. On the other hand, if kinetic energy is reduced, melt film will break apart in the secondary droplet formation. Consequently, atomization pressure decreasing or the use of reducing gas are both optimal strategy for pores reduction. Image analyses of powder cross section is unreliable and time-consuming techniques for voids quantification. In fact, huge amounts of images (and particles) would be required to obtain reliable % pores. For this reason, once

assessed pores presence, He-Pycnometry was performed to evaluate the Skeletal density of the powders. % of pores could be calculated by the difference between True density of 304L produced by LPBF in literature [98].



Figure 3.11: Comparison between OM/SEM Image Analyses method and He-Pycnometry for density quantification in run-1a\*.

A comparison between OM/SEM Image Analyses method and He-Pycnometry for density quantification were performed in run-1a\*. In Figure 3.11, results are shown. Up to D < 75  $\mu$ m both techniques seem to predicts similarly voids quantification. For comparison with literature [98], skeletal density values for AISI 304L produced by LPBF is red-marked. From D > 75  $\mu$ m on, OM/SEM Image Analyses become more and more inaccurate. For this reason, run-1b, 2a, 2b and 3 were tested by only He-Pycnometry method.



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Figure 3.12: Skeletal density analyses by He-Pycnometry on AISI 304L produced by PSI Hermiga 100. In inset, some example of particles population with and without pore.

From Figure 3.12, skeletal density analysis is divided in 3 different zones. There are 3 different trends, red-marked in Figure 3.12, for all runs. Skeletal densities vary as function of size class. For all runs in zone I, from the finest powders up to class  $53 > D > 63 \mu m$ , density grows slightly from  $7.81 \pm 0.02$  to  $7.85 \pm 0.03 \text{ g/cm}^3$ . However, in zone II, from class  $53 > D > 63 \mu m$  to  $75 > D > 106 \mu m$ , there is a decay of the skeletal density back to  $7.81 \pm 0.02 \text{ g/cm}^3$ . This decay is more evident for high-pressure run (run-3), as modeled by literature [63], respect to the others. Finally in zone III, a drop in skeletal density is evident and reported for all runs. Despite run-1b and 2b should be produced by the same atomization process parameter, even He-Pycnometry highlights a huge difference between them. A probable drop in die pressure could be happened during run-2b, as suggested by He-Pycnometry test, Yield calculation and PSD analyses.

### 3.1.2.3 Morphological Analyses

As described previously in "Chapter 1", Particle dimension is not the only functional feature required to AM powder. Morphological properties are fundamental for powders packing capacities and for their spreadability. This study was necessary to evaluate the particles shape changes associated with the GA process parameters across various size classes. For this reason, all runs were characterized by automatic-shape calculator as described in "Analytical Methods" chapter. As illustrated in Figure 3.7, 90% of the particles have a diameter < 20  $\mu$ m as evident by numerical PSD. Hence, suitable new size class need to be identified. It was chosen to use 1  $\mu$ m as lower limit of detection. Then, 1-20  $\mu$ m range was divided by two. Dimension parameter D was replaced with Circular Equivalent Diameter (CED) as explained in "Analytical Methods" Chapter. Finally, 4 size class were selected for morphological analyses: CED < 1  $\mu$ m, 1 > CED > 10  $\mu$ m, 10 > CED > 20  $\mu$ m and CED > 20  $\mu$ m. Dimensional classes were studied as function of frequency and a shape-descriptor parameter. In Figure 3.13, some examples of different dimension and shape values for similar particles are illustrated.



Figure 3.13: Comparison between shape-descriptor parameter and dimensional-descriptor parameter in numerical evaluation.

Among all the morphological parameters, the AR was chosen because it is the simplest shape factor that can be calculated. It is directly correlated to circularity [99]. In addition, it is the least affected by the magnification used for the measurements. Haferkamp et al. [100], in an investigation on 316L powders, affirm that beyond 0.8 of AR there is no further improvement in the spreading behavior of powders. 0.8 and 0.6 % of AR were chosen as parameters to segregate the particle shapes in order to be comparable. Graphs were then plotted using mixed classes of CED & AR values for an easier 2D visualization. A comparison between AISI 304L powders produced by Hoeganas through Water Atomization (WA) and GA homemade produced powders was carried out.



Figure 3.14: Mixed dimension-shape class vs frequency; analyses of the variation of highspherical particles in as function of particles dimension.

As can be seen in Figure 3.14, powders produced for WA are the least regular (i.e. distant from 1, which represents conditions of symmetry between the two diagonals of the ellipse circumscribed to the particle) as foreseen by the literature [61,63,100]. Therefore, all the runs produced show an AR higher than WA powders with the exception of powders with CED < 1  $\mu$ m, as illustrated in Figure 3.14. This happens due to the optical limits of the instrument. Very small powders are closely approximated to spheres despite their non-circular shapes. Particles with diameter CED < 1  $\mu$ m are normally excluded from analyses due to instrument limitations [101].

### 3.1.2.4 Chemical Analyses

The chemical quality of the powder largely depends on the quality of raw material. Anlayses results were compared to the standard that defines the composition of AISI 304L [96]. LECO and EDX was performed for chemical analyses of powders. Quantometer test was unable for powder samples.

LECO analyses were performed in order to evaluate chemical impurities in powder samples. C, S and N were measured and compared to ASTM A240 [96]. Tests were performed as descripted in "Analytical methods" chapter.



Figure 3.15: LECO results for: a) C concentration (%) evaluation b) S concentration (ppm) evaluation. In both cases, Run-3 results exceeded ASTM A240 values. 3 size classes were analyzed for each run

In Figure 3.15 are reported results from C & S LECO analyses. From Run-1a\* to Run-2b, all values were acceptable respect to ASTM A240. Run-3 values exceeded standard one. For this reason, Run-3 was not considered adequate for further analyses. The high concentration of C & S in this Run was attributed to a different raw materials composition. No other root cause was detected.

 $N_2$  is still considered critical for AISI 304L. A high concentration of  $N_2$  could be influenced austenite phase formation or nitride precipitation. For this reason, N LECO analyses were performed.



Figure 3.16: LECO results for N concentration (%) evaluation. No runs exceed the ASTM A240 limit. 3 size classes were analyzed for each run

As could be seen in Figure 3.16, no runs exceed the N<sub>2</sub> limits set by standard [96]. Therefore, run from 1a\* to 2b were considered accetable to further investigation. Even if O<sub>2</sub> and H concentration is not provided by standard, analyses were performed. In Table 5 results are shown. Due to high cooling rate during the atomization, elements segregation could occur inside particles. As consequence, EDX tests were carried out in order to qualitative evaluate the elements distribution into the powders. EDX tests were performed as descripted in "Analytical methods" chapter. Test were conducted in run-1a\* as reference for al runs. D <  $20\mu m \& D >$ 

106  $\mu$ m size classes were chosen because are considered the maximum and minimum dimensional cases. In Figure 3.17, D > 106  $\mu$ m size class was compared to literature [88] for powder chemical segregation.

Size class	Run-1a*		Run-1b		Run-2a		Run-	Run-2b	
	0	Н	0	Н	0	Н	0	Н	
	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	
<b>D</b> < 20 μm	0.0732	24	0.064	19.8	0.0694	21.9	0.0709	21.9	
45 > D > 53 μm	0.0289	5.26	0.0407	11.7	0.0319	3.55	0.0511	13.3	
D > 106 µm	0.0148	3.52	0.0171	4.84	0.0252	3.57	0.0143	1.93	

Table 5: LECO results; H (%) concentration and O (%) concentration. 3 size classes were analyzed for each run.



Figure 3.17: EDX map for elements segregation analyses: a)EDX maps from literature on gas-atomized powders of martensitic stainless steel (FeCrNiBSiNb) [88]. b) EDX maps carried out on run-1a\*( $D > 106 \mu m$ ) particle cross-section. In both cases, Si seems to segregate at particles surfaces.c)  $D < 20 \mu m$  particles surface. Composition seems to be homogeneous.
As could be seen in Figure 3.17.a, in literature [88] an evidence of chemical segregation in GA powder is already present. Si is normally segregated to powder surface due to its high oxygen affinity. For this reason, it could be found as oxided forms, frquently mixed with Mn (if present). Also in our study (Figure 3.17.b), Si appear to be abesnt in powders chemichal composition. By contrast, Si island seems formed at powder surface. D < 20  $\mu$ m particle surfaces are free of Si segregation. In addition, no oxides were detected as shown in Figure 3.17.c.

X-ray diffractometry tests were carried out to identify phases present within the powder. XRD anlyses were performed as descripted in "Analytical Methods" chapter. The raw material (round bars) was used as a reference. In Figure 3.18, diffraction patterns of all runs are illustrated.



Figure 3.18: XRD diffraction patterns; comparison between diffraction patterns of all runs and raw materials (taken as a reference).

As noted in Figure 3.18, all powders have both austenite peaks (gamma phase with main peak at 43.3°) and ferrite peaks (delta phase with main peak at 45°). According to the model of Cr and Ni equivalents, with the given composition, the delta phase should be inhibited with the exclusive formation of the gamma phase [85] under equilibrium condition. This is visible in raw materials. As consequence of the high cooling rate developed during atomization process, phase composition is different respect to under equilibrium solidificated samples (raw materials). In Figure 3.19 a zoomed pseudobinary phase diagram under equilibrium condition is illustrated [101]. Pseudobinary diagrams are developed from ternary ones fixing an element with a certain %. The other 2 element variables are free to change. This kind of approach is very useful for three-elements based alloys as AISI 304L.



Figure 3.19: Pseudobinary 400-1600 °C zoom phase diagram Fe-Cr-Ni under equilibrium condition [101].

As could be seen from Figure 3.19, diagram is focused on 400-1600 ° C in order to highlight the possible solidification path of AISI 304L as function of Cr/Ni ratio. Cr/Ni ratio is a critical parameter for Stainless Steel (SS) for phases formation [85]. Since chromium and nickel are strong delta ferrite and austenite stabilizers, respectively, the solidification mode in SS is often determined through the ratio of chromium to nickel equivalencies ( $Cr_{eq}/Ni_{eq}$ ).  $Cr_{eq}/Ni_{eq}$  could be calculated with many different formulations to take into account of several elements as descripted by Korinko et al. [102]. WRC equations were used as followed:

$$Cr_{eq} = Cr + Mo + 0.7 Nb$$
  $Ni_{eq} = Ni + 35 C + 20 N + 0.25 Cu$ 

In Table 6, values measured by Quantometer for massive samples are noted.

Table 6: Elements concentration and Creq/Nieq for raw materials massive samples analyzed by Quantometer.

	Raw Materials
Cr	18.0
Ni	8.0
Мо	0.35
Nb	0.02
Cu	0.47
С	0.02
Ν	0.08
Creq	18.2
Ni <sub>eq</sub>	10.6
Cr <sub>eq</sub> / Ni <sub>eq</sub>	1.72

As modeled by Welding Rresearch Council (WRC) equation [103], a  $Cr_{eq}/Ni_{eq}$  equal to 1.72 means a ferrite-to-austenite (FA) solidification path. Both massive samples and powders should be completely austenitic phased. However, due to a high cooling rate, delta ferrite were developed. Consequently, ferrite peaks are correlated to the variation from equilibrium condition. Moreover, cooling rate is strictly related to particle dimensions. The more particles diameter decreases, the higher cooling rate, it is reasonable to assume that the smaller size fractions are approaching an AF solidification mode whereas the large particles are solidifying

as FA. Ferrite main peak  $\delta(110)$  is present in all runs, as shown in Figure 3.20. However, run-1a\* shows the most high values of  $\delta(110)$  peak. This could be associated to very fine particles introduced by mixing main hopper products with secondary hopper ones. To validate this assumption, principal and secondary hopper powders were separately analyzed for run-1b.



Figure 3.20: XRD diffraction patterns of powders collected in secondary or principal hopper for run-1b. Secondary hopper contains more fine powder ( $D < 10 \ \mu m$ ) with high specific surface. Due to higher specific surface respect to bigger particles ( $D > 20 \ \mu m$ ), FA solidification path is inhibited and replaced by FA ones.

Diffraction peaks (Figure 3.20) obtained from the analysis of fine (secondary hopper) and coarse (principal hopper) powders for run-1b are shown. Ferritic phase is always present and evident in particles coming from the secondary hopper. On the other hand, austenite (111) peak is significantly reduced compared to powders coming from the principal hopper. This could be caused by a lower cooling speed. The presence of ferritic phase can also be associated with the reuse and recycling

process of powders [104]. In that case, austenitic phase is reduced by a lower concentration of austenit element promoters. In fact, Si and Mn segregates to the surface of particles which produces mixed oxide, as shown in Figure 3.21.



Figure 3.21: Si-Mn mixed oxide islands on the surface of recycled powder; adaption from [25].

### 3.1.2.5 Rheological Analyses

Rheological analyses were carried out on powders to evaluate their flow behavior. The principal techniques were developed following the growth of the powder metallurgy industry from '40. Consequently, some tests evaluate stresses not specific to AM technologies. However, it is possible to obtain comparative informations, which are useful for understanding their ability to create bulk compact or their ability to spread.

GA produced powders were evaluated by Apparent, Packing and Tap density as described in "Analytical Methods" chapter. In Figure 3.22 are illustrated Apparent and Tap densities results.



Figure 3.22: Apparent and Tap density of AISI 304L GA produced powders and comparison with commercial products.

As illustrated in Figure 3.22, the rheological characteristics of the different runs are almost identical. The graph shows that there are no variations regardless of GA process conditions. In addition, packing density values have a stable trend at around  $0.53 \pm 0.01$ .

GA home-made powders values were also compared with commercial products ones. Both Hoeganas [105] and Sandvick [106] products show similar compact behavior respect to GA home-made powders. For this reason, bulk compact powder bed could be built by home-made powders as well as commercial ones. From flowing point of view, compressibility index (CI) and Angle of repose (AoR) were tested to assure powders spreadability. Funnel Test (Hall and Carney) were performed to understand the ability of the powder to flow in a free stress state.



Figure 3.23: Results from Compressibility index and Angle of Repose tests in order to evaluate flowing performances for AISI 304L GA produced powders.

An almost constant spreadability features from 1a\* to 2b is evident in Figure 3.23. However, run-1a\* is the least spreadable run over the all. This characteristic could be associated to an higher presence of fine powders (D < 10  $\mu$ m). High CI is associated to a good compaction of powder and so, a poor spread property. In addition, high AoR values correspond to an high agglomeration tendency. No trend in flowing behavior could be correlated to GA process parameters. Furthermore, all runs failed to flow in any funnel (Hall/Carney).

Finally, Hausner Ratio (HR) was calculated as descripted in "Analytical Methods" chapter. HR is used to defined flowing behavior class. Also in this case, GA homemade powders products were compared to commercial ones as shown in Figure 3.24.



Figure 3.24: Hausner ratio values comparison between GA home-made produced powders and commercial ones.

HR of produced powders are comparable with Hoeganas [105] and Sandvick [106] ones. Powders move from "Good/free flow" zone to "Passable" zone. Both zones could be acceptable for LPBF production. In view of the previous analyses, run-1a\*, 1b, 2a and 2b can be considered suitable for LPBF processability.

# **3.2 Characterization and Feasibility by Additive Manufacturing: State of the Art**

304L has been studied using different AM techniques ranging from Direct Energy Deposition (DED) [107], to Wire Arc Additive Manufacturing (WAAM) [108–110] and Laser Powder Bed Fusion (LPBF) in order to evaluate its mechanical and microstructural characteristics as a function of the forming process.

For example, Smith et al. [107] studied and compared fatigue life of AISI 304L produced by Powder-DED with wrought one. Rectangular boxes were built up by a LENS 750 workstation equipped with 400 W Yb-Fiber Laser. Blocks were deposited on 5 mm thick wrought 304L austenitic stainless steel plate and then machined by CNC machine. DED fatigue life reflects the wrought ones when massive samples with a high relative density > 98.5 % were obtained. Two kinds of defect were observed in DED materials: in >98.5 % density samples small equiaxed pores were found. In <98.5 % lack of fusion pores with irregular shapes were found. Even though, equiaxed pores do not influence Ultimate Tensile Strength (UTS) and Fatigue Cracks Growth (FCG). Consequently, DED high density samples are comparable with wrought products. On the contrary, in low density (relative densities <98.5 %) samples, UTS and FCG decrease compared to wrought ones as function of lack of fusion presence.

On the other hand, in the case of Wire-DED products [108–110], the influence of the building direction and microstructural variation on the mechanical properties was noted. Tarasov et al. [108] analyzed how the heat input influences the phase content and the microstructural composition of 304L produced by Wire-feed Electron Beam Additive Manufacturing (W-EBAM). Samples were built up with 1 mm 304L wire on a 304L substrate and then machined. Austenite and ferrite contents were measured in order to evaluate the phase composition and evolution of the produced samples. In welding process, as function of Cr/Ni ratio, two principal crystallization mechanisms, such as primary austenite dendrite (AF mode) or primary ferrite dendrite growth (FA mode) happen. In that case, FA mode was controlling solidification process. Consequently, an austenite matrix with interdendrites ferritic crystals are obtained. As heat input increases, an increase in ferritic phase was reported. By contrast, inconsistent trend of mechanical properties was noted as function of microstructural changes. Indeed, other effects could

modify Ultimate Tensile Strength (UTS) and Yield Strength (YS) like residual stresses and grain dimensions (as modeled by Hall-Patch formula). Composition, microstructure and process condition should be controlled as function of desired goal. Moreover, growing direction highly affects WAAM products. Laghi et al. [109] correlate building direction with mechanical anisotropy. Despite similar solidification path to W-EBAM [108] samples were achieved, building direction heavily affects mechanical behavior. Transversal (T), Diagonal (D) and Longitudinal (L) samples were produced respect to the building direction by machining from massive boxes. They were tested to analyze anisotropy grade and compare with LPBF and wrought samples. WAAM samples UTS is comparable with wrought one while YS is even 55% higher in all directions. WAAM Young's Modulus (E) is 228, 129 and 105 GPa in D, L and T directions, respectively. By contrast, a mean of 195 GPa is recorded for wrought samples. LPBF samples perform better than WAAM and wrought ones due to finer microstructure. Same results were obtained by Gordon et al.[110]. They reported similar E values for T and L building directions and associated this variation to the preferential growing of the samples. Directions <200> and <010> Fe single crystal possess an E value of 125 GPa, similar to WAAM T (138.5 GPa) and D (131.39 GPa) values. XRD diffraction pattern confirm a significant crystallographic texture.

## 3.2.1 Feasibility by Laser Powder Bed Fusion: State of the Art

Considering LPBF as reference, several studies on 304L have analyzed the effects of this technique on products. However, as explained in Chapter 1, a huge number of parameters need to be checked in LPBF production. Some simple formulas, like Volumetric Energy Density, have been developed during the years but no one could model complex phenomena as LPBF techniques. For these reasons, no transferability could be assured from one system to another.

A first approach to 304L production by LPBF was conducted by Abd-Elghany et al. [111]. In their work, 304L commercial gas-atomized powder was tested on M3linear machine, provided by Concept-Laser, equipped with 95 W laser power and 0.2 mm focus diameter. The effect of process parameters on densification was analyzed varying two different scanning speeds, 70 and 90mm/s, and three layer thicknesses, 30, 50 and 70  $\mu$ m. A complete austenitic structure was obtained but a low relative density was reached (< 95 %). As consequence, UTS and YS were reduced by pores presence more than 34% and 10%, respectively. Guan et al. [112] confirmed the positive effect of LPBF production on tensile properties once near

fully dense samples were obtained. A self-developed SLM system (LSNF) with 200 W laser power and 0.1 mm beam spot was used to verify how Layer Thickness ( $L_t$ ), Hatching Distance (H<sub>d</sub>), building orientation and rotation between layer affect samples production. Lt does not influence tensile properties from 20 to 40 µm but rather modify surface roughness. With more than 40 µm Lt, it was impossible to build up samples. Also H<sub>d</sub> has a limited effect on tensile properties. On the other hand, both building orientation and rotation between layer affect heavily samples mechanical properties. As already reported for other kind of AM techniques [108,110], also in LPBF samples building direction influences UTS, YS and Elongation at Break % (A%). However, they are just lightly influences with variation below 10%. Surface roughness effects were deeply studied by Lee et al.[113] for its correlation with fatigue properties. 304L tensile specimens were produced by an EOS M290 with Lt of 20 µm, Hd of 90 µm, Scan Speed (v) of 1083 mm/s and Laser Power (P) of 195 W. Surface roughness was evaluated as function of both recoating and gas outlet directions. However, no significant statistical results were found. By contrast, fatigue rupture could be influenced by surface features and by the fatigue regime. While no effect from surface roughness for low frequency fatigue loading was noted, cracks initiation was extremely dependent on surface roughness at high frequency fatigue loading. Hence, post-processing treatments are required for specific application. This requirement is confirmed by Song et al. [98] for high strain-rate applications. AISI 304L Kolsky bar specimens were produced by a self-developed 2kW laser LSNF. The experimental results showed that the AM 304L stainless steel exhibited higher YS and flow stresses than the wrought material when the strain magnitude was less than 30%, in both compression and tension. Therefore, wrought and AM are interchangeable in high strain-rate application. In the last biennium, an increase quantity of papers were focused on the relation between LPBF process parameters, microstructure and mechanical properties of 304L [105,106,114,115]. Feasibility of 304L by LPBF was tested on several machines. Nguyen et al. [105] used a 3D Systems, ProX-300, having a 500 W Ytterbium laser achieving 99.99 % of relative density with 200 W as laser power. Hou et al. [115] produced and characterized samples through EOS M290 with 220 W setted laser power. A 99.5 % relative density cubes were produced and analyzed. Both of them [105,115] found  $\delta$  and  $\sigma$  phases after LPBF production. Whereas Ghayoor et al. [106] identified and detected just  $\delta$  phase in cubic samples produced by ORLAS Creator Metal 3D printer equipped with 250 W Yb:YAG fiber laser. AISI 304L is a fully austenitic stainless steel in wrought condition.  $\delta$  and  $\sigma$  phases are normally avoided by heat or cold-working treatment since prevent brittle behavior [116]. In LPBF samples, both  $\delta$  [106] and  $\sigma$  [115] phases were detected by XRD analyses. In LPBF samples,  $\delta$  phase is ascribed to Si-Mn oxides nanoparticles formation caused by oxygen available in building

chamber. As consequence of Si and Mn depletion of the matrix, which are austenitic promoter elements, ferric solidification is promoted.  $\sigma$  phase formation is still not completely understood.

On the other hand, those phases are formed at grain boundaries hence dislocation motion is inhibited. As consequence, strengthening effects are provided. By contrast, phase evolution needs to be accurately controlled during components working life. Another strengthening mechanism of 304L is the martensite formation after cold-plastic deformation. Ferreri et al. [114] evaluated by in-situ high-energy X-ray diffraction martensite evolution as a function of macroscopic strain during a compression test. Crystallographic texture influenced the rate at which strain-induced martensite formed in as-built AM 304L. Moreover, building orientation had a strong influence on final weight percentages of martensite. Consequently, accurate production evaluations are necessary to assure 304L feasibility by LPBF. In addition, the influence of  $L_t$  on cubic samples production has not been clarified by literature. Consequently, the role that  $L_t$  plays in sample densification was assessed.

## 3.2.2 Concept Laser Mlab Cusing R

A lack of knowledge is still present in scientific literature about AISI 304L production by < 100 W laser power LPBF machine. For these reasons, 304L cubic samples were produced by Concept Laser Mlab Cusing R equipped by 100 W Yb fiber laser with a nominal laser spot of 50 µm, continuous scanning speed up to 7000 mm s<sup>-1</sup>, and layer thickness ranging from 5 µm on. The internal building chamber had a dimension of 100 mm × 100 mm × 100 mm. Building platform was maintained at room temperature because no heating system was provided. Scanning strategy was set "island" or "check-board", as suggested by machine producers. Meander exposure was selected with 1 mm<sup>2</sup> per each island, 1 mm of y-axes shift and rotation of 90° between each layer. AISI 304L powders were produced, as already mentioned, by an Hermiga 100 PSI GA. Powders used were sieved in 20-53 µm range before introduce them in LPBF machine. All runs approved (run-1a\*,1b,2a,2b) for chemical, physical and rheological properties were mixed together. Machine producers do not provide any parameters for 304L production. Consequently, two different approaches were used: firstly, literature analyses were performed in order to obtain values for P, v, H<sub>d</sub> and L<sub>t</sub>. No papers currently define process parameters for a Concept Laser Mlab Cusing R. Although, machine producers defined a set of parameters for AISI 316L [117]. Moreover, some research is present in literature studying about the 316L production by Concept Laser Mlab Cusing R [118]. 304L and 316L chemical compositions are very similar. 316L has from 2 to 2.5 % of Mo to increase pitting resistance and an equal Ni increasing to assure austenite stability [116] respect to 304L. Therefore, a Single-Scan Track (SST) approach was followed to obtain AISI 304L process parameters starting from 316L once.

## 3.2.3 Single-Scan Track approach

LPBF process parameters were obtained by SST approach. A single scan track is defined as the formation of a single track exposed to the laser beam during one scan on a powder mono-layer. The use of SSTs is a popular and widespread method in the scientific literature [119–123] for the identification of the optimal process windows. Initially, it was developed for the analysis of weld seams, which are evaluated in cross-sections. It was subsequently adopted to evaluate the interaction of powder-substrate in AM technologies [124]. Even though cross-sectional analyses are the only way to investigate the interface between SST and substrate, on-top methods are used instead to identify P, v and H<sub>d</sub> as building parameters in LPBF machine.

SST approach is used since the early 2000s. Childs et al. [119] for first evaluated the formation of SSTs by cross-section, on-top and weight measurement. They produced single tracks by CO<sub>2</sub> laser scanning on GA bed. Solidified tracks were then removed from platform, weighed and sectioned. Five different track shapes were identified from weak stability of the track to interrupted tracks passing through an optimal formation range. From 2000s to 2010s, most of AM processes has matured and developed and with them LPBF once. With the development of LPBF technology it was necessary to improve the selection speed of process parameters. This is mainly due to the fact that it started evaluating very different types of materials. From SS (316L, 904L & 17-4 PH), tool steel H13, copper alloy CuNi10 to superalloy Inconel 625, P and v were chosen by cross-section analyses of SSTs [120,121]. Evaluation took account of SSTs shape descriptors (height, width, total dimension of Heat-Affected Zone ecc.) to define suitable process conditions. Thus far, Linear Energy Density (LED) were investigated and just P and v could be selected. However, afterwards other process parameters were investigated as Lt and H<sub>d</sub> in order to move from LED to VED approach. Yadroitsev et al. [125] for example define which process parameter mostly influenced SSTs formation. They

defined P as most correlated parameter for SSTs shape prediction. Then, Lt, v and particle mean diameter were set in order of decreasing importance. On the other hand, cross-section SSTs analyses are a really time-consuming investigation. Aversa et al.[126] correlated cross-section SST shape parameters with on-top SSTs shape parameters in order to reduce analyses time. Five regimes of on-top structures were found as descripted also before by Childs et al. [119]. Moreover, H<sub>d</sub> was never correlated to SSTs investigations. Bosio et al. [127] managed to fill this gap. By measuring and analyzing the regularity and width of the track, the desired degree of overlap (OL% i.e. % of overlap between multiple consecutive tracks) can be set. The regularity of the SST is defined as the lack of interruptions or balling phenomena in the track. A greater degree of overlap will correspond to a greater energy per unit of volume (VED) during the process and consequently, a greater probability of relative densities close to 100%. In this way, H<sub>d</sub> could be chosen as OL% calculations. However, the production of a multitude of data caused the necessity of an automated approach development. Finally, Marinucci et al. [122] designed an automated algorithm for on-top shape descriptor for SSTs. The on-top width, perimeter length and roughness indexes of the SSTs were evaluated using the algorithm. Algorithm development was necessary to be able to analyze large amounts of data and to obtain values that can be influenced as little as possible by the operator. The first of the 3 indexes (Perimetral Regularity Index) was used for track regularity evaluation.

### 3.2.3.1 Algorithms development for automated analyses

For each SST, 9 images are acquired under the optical microscope with 100X magnification. Images are processed using an ImageJ script which analyzes their regularity (presence of gaps or balling phenomena within the line) and width (thickness of the track in 10 points for each image). To avoid edge effects and transition regime phenomenon distortions, script analyzed just 3 to 7 images (central part of SST). For a full automation, microscope parameters should be maintained constant. Aperture, illumination and field were then identified and set equal for the entire analyses process. After image acquisition, every image was elaborated and transformed into a binary image. For this reason, a threshold transformation was performed. The greyscale histogram of optical microscope software (Leica Application Suite X) was used to identified the threshold value necessary for binary conversion.



Figure 3.25: Steps for automated SSTs evaluation process. a) grey values histogram from Leica Application Suite X software. b) Binary transformation to obtain black/white images. c) definition of Region Of Interest by ImageJ on AISI 304L SST. d) perimetral regularity index calculation used for SSTs automated analyses. Image adapted form [122].

As shown in Figure 3.25.a, the relative minimum between two main peaks of greyscale histogram was used. Binarization process helps to remove platform substrate from SST analyses. Once Figure 3.25.b transformation was applied, in each image Region Of Interest (ROI) was defined. ROI was used for SST regularity evaluations (Figure 3.25.c). Closed-profiles were selected as first regularity parameter. If more than one closed-profile was detected by the software, discontinuity was identified and then, SST was discarded from the analyses. By the way, not all the closed-profile SSTs could be classified as regular. For this reason, one regularity index, as defined in literature [122], was used for track regularity.

Perimetral Regularity Index =  $P_{real} - P_{ideal}$ 

where  $P_{real}$  is the real ROI perimeter, calculated by ImageJ software and  $P_{ideal}$  is obtained as the sum of V1, V2 and 2L according to the scheme reported in Figure

3.25.d. The vertical segments are calculated as the difference between the y-values of the upper and lower borders considering their first points (V1) and their last points (V2). Moreover, the ROI length, referred to as L, is calculated as the distance between the x-values of the midpoints of V1 and V2. It is clear that a smaller index value in pixel implies a greater SST regularity. Conversely, a high value of this index could indicate SSTs affected by balling.

## 3.2.3.2 Process parameter selection

Process parameters were investigated as follow: P values from 65 to 95 W with 15 W as step, v values from 400 to 1400 mm/s with 200 mm/s as step. An  $H_d$  range was calculated after SST analyses. In Table 7, the investigated process window were listed from 1 to 18. 19 and 20 conditions were chosen in order to compare 316L process parameters in Concept Laser Mlab Cusing R.

Table 7: SSTs process parameter investigation during first job. A wide range tests were performed in order to investigate as much as possible P/v process space.

	SSt JOB 1	
Condition	Power (W)	Scan Speed
	(**)	(11111/3)
1		400
2		600
3	~ <b>-</b>	800
4	65	1000
5		1200
6		1400
7	80	400

8		600
9		800
10		1000
11		1200
12		1400
13		400
14		600
15	05	800
16	95	1000
17		1200
18		1400
19	90	600
20		1200

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Platform used for analyses was a circular slice of atomization raw materials (round bar). The use of 304L round bar was proposed to avoid any interaction between materials with different chemical composition. Platforms were cut, machined and polished with 1200 SiC paper. Powder is mixed in a ratio of 1 to 10 by weight with Ethanol (EtOH) to create a slurry in order to facilitate powder spreading. With EtOH it is necessary to use the smallest possible quantity of powder and to assure the powder's adhesion to the surface during the movement of the platform into the AM machine. The platform is dried in an oven to eliminate all EtOH. In this way, a single layer of powder is adhered to the surface. Consequently, only the interaction effect between powder, laser and substrate can be investigated. A

monolayer of powder is spread on a platform ( $L_t = 40 \ \mu m$ ) using a specially developed manual recoater.

According to Bosio et al. [127] the percentage of overlap (OL%) between one laser track and the next one must lie within a range between 0 and 20%. Higher overlapping could cause an excessive amount of energy which would lead to the formation of porosity caused by trapped gas.

3.2.3.3 SSTs Results

SSTs were produced in a wide parameter window. The first process window was evaluated exclusively for powders of run-1a\*. Table 8 shows the results of this test.

		Scan Speed (mm/s)						
		400	600	800	1000	1200	1400	
ver (W)	65							
Ром	08							

Table 8: First SSTs on-top evaluation job analyses on production parameters window for run-1a\*

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The SSTs with power below 95 W are discontinuous and various irregularities occur. Among the SSTs produced with 95 W power, the continuous and regular traces were produced at a speed ranging between 400 and 600 mm/s. The search was intensified in the area with a higher number of regular and continuous SSTs in order to permit a further screening. A fine-tuning step was carried out, thereby allowing for P values between 90 and 95 W and v values between 200 and 600 mm/s (with 100 mm/s as step size). As consequence of rheology test, it was decided to process both run-1a\* and run-2b in order to evaluate the most and the least flowable powders, as descripted in "Rheological Analyses" paragraph. Four repetitions for each SST condition were performed. A/B repetitions was evaluated to avoid the effect of positioning inside the platform. C/D repetitions were performed to understand the effect of spreading. In Figure 3.26 A/B/C and D samples and their perimetric analyses a), b), c) and d) are illustrated.



Figure 3.26: Samples A/B/C/D and a), b), c) and d) automated SSTs on-top evaluation results. Results are plotted using Pixel as unit for a comparison between process parameters conditions.

Regularity index was calculated using Pixel as unit to compare perimeter of SST conditions. Conversion to  $\mu$ m was then not necessary. The algorithm automatically discarded discontinued SSTs marked them in red. Consequently, full red bars mean that discontinuity were so much to make impossible the perimeter evaluation. As consequence, every condition that was at least once red marked, was avoided. Conditions which passed discontinuity test were then evaluated by perimetric index. Condition 1-2-7-8-9-13-14-15 and 16 were then compared. V values of 6 out 9 "passed" tracks are in the 400-600 mm/s. For this reason, 400-600 mm/s was investigated in fine-tuning steps as v values. Moreover, both macro and microballing phenomena appeared during SSTs production. As can be noted in Table 9, if P < 95 W, perimetric evaluation could be affected by micro and macro-balling. Hence, Fine-tuning process parameters window was investigated between 90-95 W and 400-600 mm/s. In addition, 200 mm/s were added to the fine-tuning window. V values were then divided in 100 mm/s step in order to increase sensitivity across the process parameters window.

		Scan Speed (mm/s)								
		200	300	400	500	600				
Power (W)	06									
	95									

Table 9: Fine-tuning SSTs on-top evaluation of process parameter window for run-1a\*

		Scan Speed (mm/s)						
		200	300	400	500	600		
'er (W)	06					Constant - and a constant		
Pow	95							

Table 10: Fine-tuning SSTs on-top evaluation of process parameter window for run-2b

As can be appreciated in Table 9, all traces are regular and continuous. Where regularity is not present, the substrate is melted which indicates a lack of powder (spreading problems) rather than a processability issue. Through the algorithm, the width of the track was measured in order to identify the proper  $H_d$  needed for the production of the cubes. However, along the perimeter of the SST, microballing phenomena appeared, i.e. the formation of microspheres adhering to the outline of the trace, which actually hinder its dimensional evaluation. This phenomenon was initially attributed to secondary hopper powders present in run-1a\*.

Table 10 shows the micrographs of SSTs produced with run-2b powders. Again, all traces are regular and continuous. Where regularity is not present, the substrate is melted which indicates a lack of powder (spreading problems) rather than a processability issue. The phenomenon of micro-balling is still present and also accompanied by sputter particles around the track. As consequence, micro-balling phenomenon seems to be related to the chemical composition of 304L rather that to PSD or dimensional aspects. For this reason, run-1a\* and run-2b were considered adequate to LPBF production. <u>*All runs were then mixed together*</u> in order to produce massive cubic samples.

In both cases (run-1a<sup>\*</sup> and run-2b), it was possible to evaluate the size of SSTs. Therefore, OL% approach was applied to calculate a possible  $H_d$  value. The results are shown in Table 11.

Width	Hd/OL5%	<i>Hd/OL10%</i>	Hd/OL15%	Hd/OL20%
(PIXELS)	(µm)	(µm)	(µm)	(µm)
75	71	67	64	60
71	67	64	60	57
75	71	67	63	60
93	88	84	79	74
97	92	87	82	77
81	77	73	69	65
87	83	78	74	70
Mean	Mean	Mean	Mean	Mean
(PIXELS)	(μm)	(μm)	(μm)	(µm)
83	79	75	71	67

Table 11: Evaluation of OL degrees after width calculation for AISI 304L. Conversion between  $\mu$ m and pixel were calculated using 0.457 values. It derived by magnification degree used during image acquisition.

Through algorithm analysis, an appropriate  $H_d$  for the material was chosen.  $H_d$  value was set as 5% OL. 70 or 80 µm could be a reasonable choice for  $H_d$ . By contrast, 80 µm was chosen due to the similar values previously detected by literature evaluation for 316L. As already mentioned, once the processability of the different runs had been confirmed, they were considered and processed as a single batch of powder.

## 3.2.4 Cubic samples produced by LPBF

Two different cubic samples batches were produced with the same parameters except for  $L_t$ . The first job of cubic samples was manufactured with  $L_t = 25 \ \mu m$ , as suggested [117]. A second job with identical parameters was performed for repeatability measures. Finally, a third job was built with  $L_t = 15 \ \mu m$  to assess the influence of  $L_t$  on samples production. Samples were named as follow: A\_X for the first job with 25  $\mu m$  as  $L_t$  while B\_X for a second job with 15  $\mu m$  as  $L_t$ .

P was selected as suggested by SSTs analyses as 95 W. 90 W was further evaluated according literature references for 316L [117,118]. V values were selected by SSTs approach between 200 and 1000 mm/s. In fact, for 95 W as P, conditions from 13 to 16 (i.e. from 400 to 1000 mm/s) were continuous and regular in all samples (A/B/C/D), as show in Figure 3.26 a), b), c) and d). 200 mm/s was added to the analyses from fine-tuning window process investigation. In Table 12, process parameters for massive cubes production were listed.

Table 12:Cubic massive samples process parameters investigated. Table could be divided in 4 process parameter window: X) with 90 W as P and 0.025 as  $L_t$  Y) with 95 W as P and 0.025 as  $L_t$  W) with 90 W as P and 0.025 as  $L_t$  Z) with 95 W as P and 0.025 as  $L_t$ 

Process Parameter Windows	Sample Code	Power (W)	Scan speed (mm/s)	Hatching distance (mm)	Layer thickness (mm)	VED (J/mm³)
	A_1		200			225
	A_2		400			113
Х	A_3	90	600			75
	A_4		800			56
	A_5		1000	0.08	0.025	45
	A_6	95	200			238
	A_7		400			119
Y	A_8		600			79
	A_9		800			59
	A_10		1000			48
	B_1		200		0.015	375
W	B_2	90	400	0.08		188
	B_3		600			125
	B_4		800			94

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	B_5		1000			75
Z	B_6		200			396
	B_7		400		198	
	B_8	95	600		132	
	B_9		800			99
	B_10		1000			79

3.2.4.1 Relative Density analyses



Figure 3.27: Evaluation of porosity by OM measurement of AISI 304L cubic samples. a)  $A_X$  cubes produced with  $L_t = 25 \ \mu m$ . b)  $B_X$  samples produced with  $L_t = 15 \ \mu m$ 

In Figure 3.27, results of relative density analyses are illustrated. In Figure 3.27.a, A\_X relative density values follow a clearly trend. As velocity increased, the relative density decreases. This statement is true both for 90 and 95 W process windows. From a technologist point of view, samples from A\_3 to A\_5 and from A\_8 to A\_10 are not considerable acceptable. Porosities % > 1 could severely compromise mechanical properties. Moreover, as VED decreases, production time

decreases improving the economic performance of the process [12]. For this reason, A\_2 and A\_7 were considered the best choice for each process window.

On the other side, In Figure 3.27.b, B\_X relative density values are shown. Samples produced with Lt = 15  $\mu$ m seem to be unaffected by velocity variation. VED values were almost duplicated respect to A\_X samples. By contrast, at same VED, B\_X have a higher degree of relative density. In addition, lower VED respect to A\_X could be used if L<sub>t</sub> is smaller. Indeed, the highest relative densities values were reached at 79 J/mm<sup>3</sup> in B\_X series compared to 113 J/mm<sup>3</sup> in A\_X series. In Table 13, the best choice process conditions for each process window are noted.

Table 13: Samples designed as best choice for each process condition window. Process parameters were chosen both for their higher relative densities values and for their lower VED values.

Process	Power	Scan Speed	Hatching Distance	Layer Thickness	VED	Relative Density		
Parameter	<i>(W)</i>	(mm/s)	(mm)	<i>(mm)</i>	(J/mm^3)	(%)		
A_2	90	400	0.08	0.025	113	$99.9\pm0.1$		
A_7	95	400		0.08	0.08		119	$100\pm0.5$
B_4	90	800		0.015	94	$99.7\pm0.3$		
B_10	95	1000			79	$99.7\pm0.2$		


Figure 3.28: OM relative density obtained using different Lt in AISI 304L building process. Results of this work are compared to [5] once. Similar machines and process parameter used should assure comparable results.

Subsequently, the influence of the  $L_t$  as VED parameter on the relative density was evaluated. A\_X and B\_X samples were compared to literature values obtained with  $L_t = 30,50 \& 70 \ \mu m [111]$ . In that work, M3linear machine provided by Concept-Laser, equipped with 95 W laser power was used. Lower scanning speeds respect to our works (70 and 90 mm/s) were tested and three layer thicknesses values higher than our values (30, 50 and 70 \ mm) were investigated.

As illustrated in Figure 3.28, as the  $L_t$  decreases the whole process window increases relative densities up to 100%. As could be seen, even at high VED values (green star), relative density values close to 99% are not guaranteed. VED is confirmed as empirical parameter which is not completely related to densification process, as discuss in Chapter 1. On the contrary,  $L_t$  seems to be strictly correlated to relative density.

#### 3.2.4.2 Vickers Hardness analyses

The samples with higher density and lower VED were included in the Vickers hardness analyses in order to evaluate a possible effect of VED and  $L_t$  on hardness. Vickers values obtained for the selected samples are shown in Table 14.

Process	Layer Thickness	VED	Relative Density	Vickers Hardness	
Parameter	(mm)	(J/mm^3)	(%)	(HV <sub>0.5</sub> )	
A_2	0.025	113	99.9	$248\pm8$	
A_7	0.023	119	100	$249\pm9$	
B_4	0.015	94	99.7	$250\pm7$	
B_10	0.010	79	99.7	$245\pm9$	

Table 14: Relative density and Hardness values of samples produced with the selected process parameters

An investigation on VED and  $L_t$  influence on Vickers hardness was performed. Results are illustrated in Table 15. There seems to be no correlation among the hardness, VED  $L_t$ . Due to the manufacturing process, however, the first layers deposited are subjected to a thermal aging cycle. This cycle is due to the heating and cooling phases produced by LPBF during samples building. Thus, the longer the manufacturing time, the greater the thermal effect on the first deposited layers. Associated with this intrinsic thermal cycling are undesirable microstructural changes [25,26]. For this reason, an evaluation of the micro-hardness on the different parts of the samples was performed. The upper surface layers, i.e., the last to be produced, were defined as "Top"; the first deposited layers, on the other hand, were defined as "Bottom". The evaluation was carried out with samples produced between very different VEDs in order to confirm the influence of the energetic parameter.

Table 15: Evaluation of hardness variation caused by forming thermal aging cycle. Top and bottom layer were investigated in order to quantify hardness variation.

Position	Sample Code	VED (J/mm^3)	Vickers Hardness (HV <sub>0.5</sub> )
Тор	B_10	79	$243\pm8$
Bottom	B_10	79	$246\pm10$
Тор	B_6	396	$241\pm5$
Bottom	B_6	396	$242\pm7$

#### 3.2.4.3 XRD Analyses

As can be seen in Table 15, there is no significant variation in hardness values. In this sense, it is possible to state that both VED and sample height do not affect the Vickers hardness. Nevertheless, to assess the possibility of phase changes, additional XRD analyses were performed. The patterns obtained from samples with very different VEDs (from 45 J /  $mm^3$  up to 396 J /  $mm^3$ ) were then compared in Figure 3.29.



Figure 3.29:X-Ray Diffraction pattern of AM samples produced with high (396 J/mm<sup>3</sup>), medium (238 J/mm<sup>3</sup>) and low (45 J/mm<sup>3</sup>) VED.

As can be seen in Figure 3.29, as the VED increases, there is almost no difference in XRD peaks. Therefore, there is no evidence of a correlation between VED and samples phase composition. Both austenitic and ferritic phases maintained constant proportion as VED changing. The tests were also carried out on samples of the same material product by Cast or Hot-Rolling (HR). Results can be found in Table 16.

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Table 16: Comparison between different forming technologies results. FWHM and Vickers micro-hardness could be related to the grain variation caused by different forming technologies.

Forming	VED	Relative Density	FWHM Left	Vickers Hardness	
Technologies	(J/mm^3)	(%)	(°2 Th.)	(HV <sub>0.5</sub> )	
AM/B_10	79 J	99.7	0.1023	$245\pm9$	
AM/B_6	396 J	99.6	0.0758	$242\pm 6$	
CAST	-	-	0.3070	$153\pm10$	
HR	-	-	0.3492	$209\pm5$	

Samples produced for AM, at any VED, are harder than samples produced using traditional technologies. HR samples show higher hardness than CAST once (209  $HV_{0.5}$  instead of 153  $HV_{0.5}$ ) due to plastic deformation hardening, which is the principal strengthening strategy for 304L alloy. The decrease of Full Width Half Maximum (FWHM), that is the width of the diffraction peak, in radians, at a height half-way between background and the peak maximum, indicates a smaller grain size with consequent strengthening for Hall-Patch by the AM samples [128]. As the VED increases, there is a further decrease in FWHM as consequence of the extremely high heating and subsequent cooling rates. Nonetheless, no modifications were noticed in the microstructure nor in the hardness of samples. Finally, it is possible to notice a decrease in the intensity of the peak at 75 ° indicating a preferential growth along the plane (111) by cast samples. XRD patterns are detailed in Figure 3.30.



Figure 3.30: X-Ray Diffraction pattern of samples produced with different forming technologies. A complete austenitic microstructure could be obtained just by hot-rolling formation process.

As illustrated in Figure 3.30,  $\delta$  (111) peak, present in AM samples, disappeared in HR once. A complete austenitic structure could be achievable just by HR forming technologies. Moreover, the absence of  $\gamma$  (220) peak in HR samples shows a preferential growth in  $\gamma$  (200) and  $\gamma$  (111) planes. In the same way, CAST sample owns a mixed austenitic/ferritic structures as AM sample. By contrast, the absence of  $\delta$  (002) and  $\gamma$  (220) could be related to preferential growth as HR samples.

## **Chapter IV**

# 4 LPBF of AlSi10Mg and new Albased alloy

## 4.1 AlSi10Mg as reference material

AlSi10Mg is one of the most studied and known aluminum alloy produced by AM. Starting from commercial products, chemical composition of Al-based alloy (AlSi10Mg) was modified. CL31, which is the trade name of Concept Laser AlSi10Mg, was studied as reference. In order to understand CL31 feasibility, cubes were produced in Concept Laser Mlab Cusing R. Relative density and Vickers hardness analyses were performed to investigate Scanning strategy role in LPBF massive production. As explained in Chapter 1, Scanning strategy is the set of 4 main parameters: exposure, scan pattern, rotation between layers and shift between layers. While the first 2 parameters are considered in-layer operation, rotation and shift are defined as out-layer operation. Among these 4 parameters, exposure, scan pattern and rotation between layers were studied. Once assessed reference feasibility, 2 new Al-based chemical compositions were investigated.

#### 4.1.1 CL31

AlSi10Mg is an aluminum alloy optimized during last 20 years for AM processes. It is commercially produced by almost all AM machine producers shaped as fine powders. It is a typical cast alloy with excellent cast-ability and weld-ability making it perfect for parts with thin wall thicknesses and complex geometries. It is used for applications where a combination of good thermal characteristics and low weight are required. Products built in AlSi10Mg can be further machined, coated and sandblasted in order to improve their surface characteristics. During this investigation, AlSi10Mg powders were provided by Concept Laser GmbH, commercially named CL31. CL31 chemical composition is described in Table 17:

Element	Weight %			
Al	Bal.			
Si	9.0 - 11.0			
Mg	0.2 - 0.45			
Fe	0.55			
Cu	0.05			
Mn	0.45			
Ni	0.05			
Zn	0.10			
Pb	0.05			
Sn	0.05			
Ti	0.15			

The amount of Magnesium is quite variable but a significant variation could be also accepted. Zinc and Titanium elements traces are sometimes present. Silicon is used to make the molten bath particularly fluid.

The percentage by weight of Silicon is well above the solubility limit in aluminum. Al-Si alloys are defined as eutectic alloys when the Si is in the range of 11-13 % wt., hypoeutectic if the Si is less than 11% wt., and hypereutectic when the Si is greater than 13 % wt. Strengthening of these alloys is generally possible, through the addition of other alloying elements, such as Mg and Cu, which make Al-Si alloys hardenable by heat treatment or by using rapid solidification techniques, in which the cooling speed is greater than  $10^2$  K s<sup>-1</sup>, which leads to a refinement of the microstructure [9]. In Figure 4.1.a) and .b) it is possible to see the OM cross-section of as-built AlSi10Mg and OM cross-section of T6 heat treated AlSi10Mg samples, respectively. In Figure 4.1.c) a detail magnified zone under SEM reveals Si segregation at  $\alpha$ -Al boundaries.



Figure 4.1: a) OM image of as-built AlSi10Mg cross-section. b) OM image of T6-heat treated AlSi10Mg cross-section. c) SEM magnification of a) revealing Si segregated on the boundaries of  $\alpha$ -Al; adaption from [129].

Cast components conventionally produced from this type of aluminum alloy are often heat treated to improve mechanical properties, for example using the T6 cycle of annealing, quenching and aging. The laser sintering process is characterized by extremely rapid melting and re-solidification. This produces a metallurgical condition and corresponding mechanical properties similar to heat-treated T6 parts.

Therefore, such hardening heat treatments are not recommended for laser sintered parts. By contrast, a stress-relieving cycle of 1 hour at 240 °C is suggested [130].

### 4.1.2 Scanning strategy analyses

CL31 analysis was performed to evaluate the effect of Scanning Strategy (SS) parameters on sample final relative densities. Two different jobs were produced by Concept Laser Mlab Cusing R. The first one, job A, was developed to assess the exposure, scan pattern and rotation between layers as SS parameters. The second one, job B, was studied to correlate VED and SS. Economical and performance evaluations were also investigated as function of VED and SS. Vickers Hardness was performed as mechanical test for scientific literature comparison. All the process parameters were derivated by Concept Laser default ones for CL31. For this reason, in job A, P = 95 W, v = 650 mm/s, H<sub>d</sub> = 0.105 mm, L<sub>t</sub> = 0.015 mm were set constant while exposure, scan pattern and rotation between layers were modified. Exposure parameter was modified passing from 1D, to 2D and finally Meander. Scan pattern was investigated starting from Full, Stripe5 and finally Island5. In the end, rotation between layers were studied choosing 3 different angles: 0 °, 67 ° and 90 °. The meaning of each SS parameters is detailed in chapter 1. A\_X samples were produced using SS illustrated in Figure 4.2.



Figure 4.2: Scan patterns, rotation angle between layers and exposures analyzed as SS process parameters [12].

In Table 18, SS process parameters were listed for each sample.

Job	Sample code	Scan pattern	Exposure	Rotation between layers [°]	Shift between layers [mm]
	IM90 °	Island5	Meander	90	1
	F1D0 °		1D		
	F2D0 °	Full	2D		
	FM0 °		Meander	0	
٨	S1D0 °		1D	0	
Α	S2D0 °		2D		0
	SM0 °		Meander		
	S1D67 °	Supes	1D		
	S2D67 °		2D	67	
	SM67 °		Meander		

Table 18: Job A Scanning Strategy parameters.

On the other hand, in job B, SS were set as "Island5" (Island/ 5 mm scan vector/ Meander/ 90  $^{\circ}$  rotation/ 1 mm shift) and "Stripe5" (Stripe/ 5 mm scan vector/

Meander/ 67 ° rotation). Scan vector length was maintained constant and equal to 5 mm so it is normally omitted. Stripe is the EOS machines default SS and then it was chosen for comparison between EOS and CL AlSi10Mg products. Job B process parameters are given in Table 19.

Ich	Sample	Р	V	Hd	Lt	VED	Saanning Stratagy									
cod	code	[W]	[mm/s]	[mm]	[mm]	[J/mm <sup>3</sup> ]	Scanning Strategy									
	IM750		750			80.4										
	IM850		850 950 650	0.105		71.0										
	IM950					63.5										
В	IM115	95		650	650								0.115	0.015	84.7	IM90 °
	IM125					0.125		77.9								
	IM135					0.135		72.2								
	IM90 °			0.105		92.8										

Table 19: Job B Scanning Strategy and process parameters variation.

		SM750		750			80.4	
		SM850		850			71.0	
		SM950		950	0.115		63.5	
	B SM1 SM1 SM1	SM115	95	650		0.015	84.7	SM67 °
		SM125			0.125	0.012	77.9	
		SM135		650	0.135		72.2	
	SM67 °			0.105		92.8		

Once A\_X samples were produced, relative density analysis was performed. Massive samples were cut, mounted and polish as descripted in "Analytical methods" chapter. ImageJ software was used to evaluate porosity presence inside samples. Results are illustrated in Figure 4.3.



Figure 4.3: Results of relative density analyses on CL31 samples built with different SS [12].

As it could be seen in Figure 4.3 there is a very clear correlation between SS parameters and relative density. Exposure has a negligible effect on densification process. For example, considering Full no rotation group, F1D0  $^{\circ}$  can be compared with F2D0  $^{\circ}$  and FM0  $^{\circ}$ . It is possible to note very few differences, taking account the high standard deviation. This trend is notable also for stripe no rotation group and stripe rotation 67  $^{\circ}$  group. Moreover, also scan pattern effect is negligible as it could be seen between FM0 $^{\circ}$  and SM0  $^{\circ}$ . In contrast with previous parameters, Rotation angle between consecutive layers strongly influenced densification process. Relative density of rotated samples reach very high values compared to not rotated ones. The reason could be found in Single-Scan Track geometrical features, as descripted by Su et al. [131].



Figure 4.4: Pores overlapping and distribution as function of Hd, Lt and SS. While SS variation is a symmetry operation, without production time changes, Hd and Lt variation could induced a great production time increasing

As can be seen in Figure 4.4, pores distribution is highly influenced by  $H_d$ ,  $L_t$  and SS. For example, if Full scan pattern and high  $H_d$  are selected, pores overlapping form columned porosity inside the sample (Figure 4.4.a). Inter-layer overlapping regimes is obtained with a low relative density sample production. intra-layer and mixed overlapping regimens can be developed by  $H_d$  and  $L_t$  variation. However, production time and, consequently, cost are compromised (Figure 4.4.b and Figure 4.4.c).

By contrast, rotation between layers introduction in SS can reduce porosity presence even at high  $H_d$  (Figure 4.4.d). Moreover, rotation between layers does not increase production time or cost because is a symmetry operation. Then, 100% relative density can be reached by a  $H_d$  optimization (Figure 4.4.e). As explained, all four rotated SS reach 99 % of relative density but from production time point of view, they are very dissimilar.



Figure 4.5: Production time variation as function of produced volume and chosen exposure. a) Stripe scan pattern b) Island scan pattern.

In Figure 4.5, the production times as function of the produced volumes are presented. Data were obtained by the simulation of samples building through CL WRX control software. Using Stripe scan pattern and growing cubes dimensions (sample side of 10, 30 or 60 mm), it could be seen that the exposure parameter modification could introduce a time saving up to 15 h (Figure 4.5.a). Same results could be noticed also for Island scan pattern in Figure 4.5.b). Rotation and shift were not investigated because did not introduce a production time increasing. Indeed, they are virtual symmetry operation.



Figure 4.6 a) S1D67  $^{\circ}$  OM image acquired at 200x after keller etching ; b) F1D0  $^{\circ}$  OM image acquired at 100x after keller etching

OM etched sample inspection reveals traces of melt pools on XZ sample crosssection, as shown in Figure 4.6. The melt pool traces of rotated samples are very different in shape and size respect to non-rotated ones. All the samples built with rotation angle between layers (90 ° or 67 °) present a configuration similar to Figure 4.6.a). Melt pool traces get growing dimensions as the mismatch angle between cross-section plane and rotation between layers angle increases. By contrast, aligned melt pools structure can be detected in non-rotated samples (Figure 4.6.b). While in non-rotated samples the spatial arrangement of the porosities is overlapped between scanning traces, in rotated ones they are arranged randomly. In addition, it can be seen that melt pool traces could own greater depth (25  $\mu$ m) respect to Lt (15  $\mu$ m). This is mainly caused by the re-melting of each layer due to the repeated passages of the laser. Finally, Vickers hardness was measured for three samples. This is due to evaluate the influence of exposure, scan pattern, rotation between layers and shift between layer on hardness. Samples were chosen among the most relative dense ones.



Figure 4.7: Evaluation of Vickers Hardness variation as function of SS parameters.

As evident from Figure 4.7, no difference in term of Vickers hardness could be noticed. However, IM90  $^{\circ}$  sample seems to own higher deviation standard respect to S\_X67  $^{\circ}$  ones.

#### 4.1.2.2 VED vs Scanning Strategy analyses

In Figure 4.8 it can be seen that the scanning speed and the hatching distance have almost the same influence on the densification process. In Figure 4.8.a), at high v, the resulting density is still higher than 99 %. The IM90° strategy has a slightly decreasing trend with an increase in v while the SM67 ° strategy maintains more constant values. The slight bend in the IM90 ° behavior could be influenced by the heat distribution which, even if the VED is kept constant for both strategies, is influenced by the scan pattern. This impacts on both residual stress and grain growth [6] and could be emphasized by high v. Density values of samples built with the IM90 ° strategy also have a greater standard deviation respect to SM67 ° ones. However, in both cases the variations in relative density can be considered negligible. Finally, moving from 650 to 950 mm/s, it is possible to achieve up to 25% time saving (54 h instead of 73 h), with cubes of dimensions 60x60x60 mm<sup>3</sup>, maintaining a relative density higher than 99%.



Figure 4.8: Influence of V (a) and Hd (b) on CL31 consolidation [12].

In Figure 4.8.b), the influence of  $H_d$  in the densification process is analyzed. Compared to v,  $H_d$  causes a more significant decrease in density for both strategies, with a comparable standard deviation between the two strategies. With cubes of dimensions 60x60x60 mm<sup>3</sup>,  $H_d$  achieve only a 17 % time saving (60 h instead of 73 h).

Finally, comparing samples having similar VED values (e. g. IM135 and IM850), the obtained results suggest that to decrease the production time and maintain a good densification it is possible to increase both the v or H<sub>d</sub>. In fact, increasing v or

 $H_d$  allows a more productive LPBF process, by decreasing the permanence time of the laser in each area. The entire process is then accelerated but 99.5 % of relative density is no more reachable. On the other hand, an acceptable value of 99 % is still maintained. Vickers Hardness was then measured to assure comparable mechanical properties.



Figure 4.9: Evaluation of Vickers Hardness variation as function of SS and VED parameters.

Also in this case, as evident from Figure 4.9, no difference in term of Vickers hardness could be noticed. IM750 sample owns higher deviation standard respect to other ones. This fact seems to not being correlated with SS or process parameters. In the end, SMX° do not strongly contribute positively on samples building respect to IMX° one. For this reason, Island5 with Meander Exposure, 90 ° rotation and 1 mm shift between layers was maintained as standard SS, such as recommended by Concept Laser.

Once CL31 was assessed as AlSi10Mg reference, new Al-based compositions were developed.

## 4.2 Al-based new composition alloys

During the last 5 years, much attention has been given to design alloying in AM sector. The main reason is the possibility to develop entirely new chemical compositions having mechanical, electrical, thermal and corrosion properties superior respect to conventional metallurgy alloys could reach. In equilibrium condition, rarely elements solid solubility exceeded 1 % at. in Al alloys. Rapid Solidification Processes (RSPs) produce alloys with increased solid solubility of elements in matrix as result of the extreme cooling rates involved in the processes.

Furthermore, elements normally used for solid solution or precipitation strengthening (such as Mg, Zn, Cu and other) have poor thermal stability. By contrast, Fe, Cr and Ni precipitates own high thermal stability but are normally avoid as Al alloying elements. This is due both their extremely low maximum equilibrium solubility and for their tendency needle-shaped precipitates forming. However, RSPs modify both these Al alloying elements features. In Table 20, equilibrium and extended solubility ranges are listed.

Solute	Maximum e solubil	equilibrium ity	Reported increased solubility		
	Wt. %	At. %	Wt. %	At. %	
Cu	5.65	2.4	40-42	17-18	
Fe	0.05	0.025	8-12	4-6	
Cr	0.72	0.44	8-10	5-6	
Ni	0.04	0.023	2.4-15.4	1.2-7.7	

Table 20: Variation of solid solubility range for some Transitional Metal elements as reported in [132]

As reported by Inoue [133], Al alloys rich in Fe, Si, Cr and Ni have been studied and developed for RSP since '70. RSPs techniques could produce metastable alloys consisting of amorphous or nano/micro-crystalline structure and which exhibit high tensile strength, good ductility, high impact fracture energy and exceptional thermal stability which have not been obtained for conventional Al-based crystalline alloys. For example, AlFeCrTi alloy was demonstrated to exhibit a Creep Strength of 350 MPa at 300 °C [134].This is an incredible goal for an Al alloy which normally could operate at 125 °C as maximum service temperature. Therefore, the use of Transitional Metal (TM) elements raise Al alloys performances up to compete with Ti alloys for high temperature uses [132]. As consequence, considerable interest could be found in the field of materials for energy production for this type of alloy.

A first approach to alloys modification by AM techniques was performed by Knoll et al. [135]. They analyzed a combinatorial method for graded bulk alloys production. The reference materials were a Cr–Mo–V hot working tool steel and a Ni-based maraging steel. Using a powder mixing chamber before the consolidation, graded structure could be achieved by Laser Metal Deposition (LMD), with varying composition from layer to layer (alloy volume fractions 80:20, 60:40, 40:60, and 20:80). In this way, it is possible to synthesize alloy compositions and microstructures that are either not at all or not readily accessible by conventional bulk alloy synthesis.

On the other hand, RSPs techniques could be used for new and impossible (for traditional forming techniques) composition alloys development for structural high temperature condition. For example, Srivastava et al. [136] used spray deposition to investigate Fe addition in Al-Si alloys. The addition of Fe in Al-Si alloys gives rise to stable intermetallic phases. Pre-alloyed powders were produced by closecoupled spray nozzle atomization. The alloy was melted in a graphite crucible, up to a 1200 °C and then atomized. While the as-cast A15Fe alloy fractured prematurely without showing any yielding, the Al5Fe spray deposited and extruded alloy showed uniform distribution of ultrafine Al<sub>3</sub>Fe phase. Al<sub>3</sub>Fe phase was attributed of the alloy brittleness. Crack propagation along the Al<sub>3</sub>Fe/α-Al interface detected, which indicated a poor interface strength. By contrast, was All8Si5Fe1.5Cu spray-formed and extruded alloy consisted of fine primary Si and refined intermetallic  $\delta$ -Al<sub>4</sub>Si<sub>2</sub>Fe and  $\beta$ -Al<sub>5</sub>SiFe phases. Ultrafine size of Al<sub>3</sub>Fe phase allows a large amount of plastic deformation and an increased strength. Rajabi et al. [137] studied the effect of cooling rate and subsequent hot consolidation on the microstructural features and mechanical strength of Al-20Si-5Fe-2X (X=Cu, Ni



and Cr) alloys. Atomization were conducted under nitrogen at 870 °C with 80 bar as die pressure to obtain fine pre-alloyed particles.

Figure 4.10: Microstructure of rapidly solidified Al20Si5Fe alloy: (a,b) gas-atomized powder; (c,d) melt-spun ribbon; (a,c) optical micrograph; (b,d) scanning electron micrograph [137].

Ni was found to be the most effective element in strength increasing. AlSiFe alloy containing Ni exhibited an improved strength due to the formation of precipitates such as Al<sub>3</sub>Ni. By contrast, Cr was found to be effective in modifying the primary Si and refining the grains. Cr also altered the morphology of the iron-containing intermetallic compounds. In addition, no significant effect of Cu and Ni on the microstructural features could be outlined. Even if other minor elements were present in the composition (Cu, Ni and Cr), the microstructure is rather similar to that of the Al-Si-Fe ternary alloy. However, the acicular intermetallic phase, present in cast microstructure, is precipitated in fine spherical shape. Shape modification of intermetallic precipitates is promoted by the high cooling rate. An example of different kinds of microstructures obtained by some RSPs can be observed in Figure 4.10. Another example of high cooling rate shape-induced variation was proposed by Zheng et al. [138]. According to them, inside the Laser Melted Zone (LMZ) of Al8.5Fe1.3V1.7Si alloy, either an extremely fine cellular-dendritic structure or a

mixture zone of the  $\alpha$ -Al matrix and nanoscaled Al<sub>12</sub>(Fe,V)<sub>3</sub>Si particles appeared. The  $\alpha$ -Al and Al<sub>12</sub>(Fe,V)<sub>3</sub>Si mixture zone was also observed in the Heat Affected Zone (HAZ), but another phase, submicron  $\theta$ -Al<sub>13</sub>Fe<sub>4</sub> particles with rectangular or hexagonal shapes, formed along the melting pool border. Powders were pre-alloyed by ZGW-10 vacuum gas atomization instrument and processed through a selfdeveloped DEYU LM 200 SLM instrument. This instrument is equipped with an Yb: YAG fiber laser, which produces a laser beam with a wavelength of 1060 nm and a spot size of 80 µm. The electron diffraction pattern of the spherical phase could be indexed to the cubic body-centered massive Al<sub>12</sub>(Fe,V)<sub>3</sub>Si phase. This desirable mixture zone of  $\alpha$ -Al and Al<sub>12</sub>(Fe,V)<sub>3</sub>Si was extremely stable, significantly contributing to the excellent alloy mechanical properties at high temperatures. Phases distribution inside the LPBFed Al8.5Fe1.3V1.7Si alloy samples could strongly influenced by LPBF process parameters. Microstructural evolution as function of VED can be noted in Figure 4.11.



Figure 4.11: Phase structures of Al8.5Fe1.3V1.7Si alloy produced by LPBF technique. Border of LMZ/HAZ is full of  $\theta$ -Al<sub>13</sub>Fe<sub>4</sub> precipitates while LMZ and HAZ presented a mixture zone of  $\alpha$ -Al and Al<sub>12</sub>(Fe,V)<sub>3</sub>Si. As function of VED, a significantly microstructural change could appear in LMZ phase microstructure; adaption from [138].

Based on the XRD and EDS results, the presence of  $\theta$ -Al<sub>13</sub>Fe<sub>4</sub> was confirmed. Morphology and dimensions of this sub-micron  $\theta$ -Al<sub>13</sub>Fe<sub>4</sub> phase changed considerably from the harmful needle-like  $\theta$ -Al<sub>13</sub>Fe<sub>4</sub> phase in the conventional ascast alloy, illustrated in Figure 4.12.



Figure 4.12: Harmful needle-like  $\theta$ -Al<sub>13</sub>Fe<sub>4</sub> phase in the conventional as-cast Al8.5Fe1.3V1.7Si alloy. Shape variation could be promoted by cooling rate.

Manca et al. [139] developed an AlSiNiFe novel composition alloy by SLM Solutions 280HL machine equipped with a 1064 nm wavelength 200 W Yb-laser. Al12Si1.4Fe1.4Ni with minor additions of Cu was produced by gas atomization at the UC RUSAL. Al, Si, Al<sub>5</sub>Fe(Ni,Cu) and Al<sub>3</sub>(Ni,Cu) phases were identified in the microstructure of as-produced samples using XRD analysis. While the size of the Al<sub>5</sub>Fe (Ni, Cu) and Al<sub>3</sub>(Ni, Cu) phases did not change significantly, silicon particles increased from 300 nm to 800 nm after annealing at 495 °C for 3 h. This is due to the high thermal stability of Al-Fe/Ni intermetallic precipitates formed during the production, especially Al<sub>5</sub>Fe(Ni, Cu) and Al<sub>3</sub>(Ni, Cu) particles.

However, not all the possible combination of elements could be produced by LPBF process. For this reason, three main strategies have been developed for improve LPBF feasibility of AM materials. Uddin et al. [140] increased platform temperature to avoid high crack sensitivity issues during solidification in 6061 Al alloys processed by LPBF. The large thermal conductivity and the high heats of fusion for 6061 Al alloy contribute to the difficulty in achieving enough undercooling. Powder-bed heating drastically reduces these thermal barriers. In this way, cracking is eliminated both for elongated and equiaxed grains. Different approaches were used by Montero-Sistiaga et al. [141] and Aversa et al. [142] which both produced 7075 Al alloys by LPBF techniques. They modified alloy composition in order to reduce melt viscosity and to hinder cracks formation. While Montero-Sistiaga mixed 7075 powders with pure Si ones, Aversa used AlSi10Mg and 7075 powders as raw materials. Their mechanical and microstructural results

were comparable and crack and pores-free samples were obtained. The last improving feasibility strategy developed for LPBF technique was studied by Martin et al. [143] which included the use of nano-particles as inoculant. They mixed H<sub>2</sub>Zr nanoparticles to 6061 and 7075 Al alloys to promote 100% relative density samples formation. Pinning effect of particles hindered cracks formation. Moreover, Al-Zr intermetallic precipitation contributed to the pinning effect providing additional strengthening and resistance to grain growth.

TM elements like Fe, Cr and Ni have been investigated for years in Al alloying design field. In this thesis, Fe, Cr and Ni were added to AlSi10Mg composition to assess their strengthening effects. Two main compositions were studied mixing AlSi10Mg and AISI 304L as raw materials for GA. The 1:8 and 1:4 weight ratios for 304L and Alsi10Mg, respectively, were used. Consequently, new compositions were named AlSi8Fe9Cr2Ni (Fe\_9 %) and AlSi8Fe18Cr5Ni3 (Fe\_18 %). Pre-alloyed powders were then used for LPBF feasibility in Concept Laser Mlab Cusing R. Unfortunately, Concept Laser Mlab Cusing R is not provided by heating bed elements and for this reason increased bed temperature strategy was dropped. By contrast, both composition modification and inoculant particles strategies for LPBF production were approached.

#### 4.2.1 AlSi8Fe9Cr2Ni

A first Al-Fe alloy were produced by GA process and then processed by LPBF. AlSi10Mg and AISI 304L ingots were cut and mixed in atomization crucible. AlSi8Fe9Cr2Ni (Fe\_9 %) composition was reached using 1:8 304L to AlSi10Mg weight ratio. As shown in Table 20, Fe solid solubility in Al is 0.05 wt. % at thermodynamic equilibrium. However, it can be increased up to 12 wt. % using RSPs. For this reason, the first Al-Fe alloy developed was set as 9 % wt. of Fe content. Pre-alloyed powders were then characterized by PSD, He-Pycnometry and XRD analyses while particle microstructures were studied via cross-section inspection by OM, SEM and EDX techniques.

Then, Single-Scan Tracks (SSTs) approach was applied for LPBF process parameters identification. Finally, massive samples were produced by Concept Laser Mlab Cusing R and investigated through OM, SEM and XRD analyses.

Pre-alloyed powders were produced by a PSI Hermiga 100 GA plant set in Alessandria site of Politecnico di Torino. In Table 21, Atomization parameters used are listed.

Table 21: GA process	parameters for AlSi8Fe9Cr2Ni	powders production.
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Composition	AlSi10Mg (Kg)	AISI 304L (Kg)	Atomization Temperature (°C)	Nozzle Diameter (mm)	Top Pressure (barg)	Die Pressure (bar)	Isothermal stage	Post- Atomization Weight [g]	Atomization Yield [%]
AlSi8Fe9Cr2Ni	1.5	0.23	1200	2.5	0.25	27.5	1 h / 1000 °C	1250	72

Atomization temperature was set quite high respect to melting temperature of AlSi10Mg (above 650 °C). This fact is due to assure the complete melting of 304L in AlSi10Mg melt. For this reason, an isothermal stage of 1 h at 1000 °C was performed. Indeed, as expected by ternary isothermal section of Al-Si-Fe phase diagram (Figure 4.13), only liquid phase is presented at 1000 °C. By contrast, at 1000 °C and under vacuum atmosphere, low-melting elements like Mg could be volatilized. Nozzle diameter, top pressure and die pressure were chosen as GA supplier suggested. 72 % of atomization yield was reached.



Figure 4.13: 1000 °C isothermal section of Al-Si-Fe ternary phase diagram; adaption from [144]. Green dot represents Fe\_9 % composition inside the phase diagram.

As already mentioned in Chapter 3, powders collected by GA main hopper were sieved. A Retsch Sieve Shaker AS200 with 20, 53 and 106  $\mu$ m of mesh sizes was adopted, as mentioned in "Analytical method" Chapter. Up to 50 % wt. was collected in 20-53  $\mu$ m which could be considered an excellent result. More than 700 g were collected respect to 500 g which could be considered the minimum quantity for LPBF production, as mentioned in Chapter 3.



Figure 4.14: a) Mass Particle Size Distribution obtain by sieving technique; b) Scanning electron microscopy image of 20-53  $\mu$ m size class of AlSi8Fe9Cr2Ni alloy. The image was acquired at 1000x

In Figure 4.14.a, the Mass PSD can be noted. Even if 20-53  $\mu$ m is the main powders size class, 53-106 and D > 106 got at least 20 % wt. which is a consistent mass fraction. By contrast, D < 20  $\mu$ m is very tiny amount of particles (less than 5 % wt.). SEM image of as-produced powders is illustrated in Figure 4.14.b. As can be seen, all particles got spherical shape as predicted by GA validation in Chapter 3. On the other hand, some particles presented two main phases: a darker one which surrounding a lighter-spotted one. Not all the particles showed this configuration.



Figure 4.15: EDX map analysis of 20-53  $\mu$ m size class particle; Fe and Cr were mainly distributed in white phase while Al seems to be concentrated in darker regions. Si is quite uniformly distributed.

EDX map analysis was performed on 20-53  $\mu$ m size class as shown in Figure 4.15. Dark grey phase is richer in Al and poorer in Fe and Cr respect to white one. Si seems to be uniformly distributed in all phases. As consequence, the white phase could be associated to Fe and Cr. Images of Figure 4.15 were obtain by BSD detector and, for this reason, low atomic weight elements appear darker respect to high atomic ones. This is not true for OM images.


Figure 4.16: OM cross-section analysis of AlSi8Fe9Cr2Ni particles in  $D < 20 \ \mu m$  size class. a) particle before etching. b) particle after Keller etching for 8 s.

As can be seen in Figure 4.16.a, OM cross-section analysis was performed on D < 20 µm size class before etching. In this OM case, in contrast with BSD images, white phase could be associated to Al while dark grey to a Fe phase. After etching (Figure 4.16.b) it is clear that almost all particle surface was etched by Keller reagent. Only rarely and small white spots (Nano metric phase) survived to the acid attack. By contrast, in Figure 4.17, a clear difference could be noted before and after etching.



Figure 4.17: OM cross-section analysis of AlSi8Fe9Cr2Ni particles in  $D > 106 \ \mu m$  size class. a) particle before etching. b) particle after Keller etching for 8 s

In Figure 4.17.a, white and grey phases could be clearly distinguished. Grey phase seems to be dominant respect to white one. After etching (Figure 4.17.b), a great amount of Fe island survived to Keller acid attack. This phase seems to be

unaffected by acid presence as Fe should be. Moreover, in XRD analyses can be noted some correlation with previous findings.



Figure 4.18: XRD analyses for AlSi8Fe9Cr2Ni alloy and phase variation as increasing particle size.  $\alpha$ -Al peaks are the most intense for all size class while  $\gamma$ -Fe peaks phase appears from 20-53  $\mu$ m size class.

As illustrated in Figure 4.18, in D < 20  $\mu$ m size class,  $\gamma$ -Fe main peak phase (44.5 °) is less intense respect to other size classes. As seen in Figure 4.16.b, D < 20  $\mu$ m size class particle was completely etched by Keller acid. This finding, associated to XRD analyses, confirms an higher relative quantity of  $\alpha$ -Al phase in this kind of particles respect to bigger ones. By contrast,  $\alpha$ -Al phase do not modify its main peak intensity over the size classes. Moreover, a metastable  $\epsilon$ -Fe phase was detected at 42 °. It is normally produced at very high pressure (Pressure > 120 kbar in unary Fe phase diagram [145]) and it is considered a precursor of  $\alpha$ -martensite phase [146].  $\epsilon$ -Fe 42 ° peak maintains constant intensity over the size classes. A wide range of intermetallic precipitates appears as diameter increased. However, just  $\theta$ -

Al<sub>13</sub>Fe<sub>4</sub> seems to be present in every size classes. Moreover,  $\theta$ -Al<sub>13</sub>Fe<sub>4</sub> (0 0 3) peak at 22.4 ° is quite intense respect to relative intensity of its XRD reference pattern 98-010-3423. It could be attributed to a preferential growth caused by LPBF process. These findings confirmed expectations since Fe\_9 % composition is in  $\theta$ -Al<sub>13</sub>Fe<sub>4</sub> solidus surface as shown in Figure 4.13. Once particles morphology microstructure and phase content were assessed, porosity content measurement was performed.



Figure 4.19: He-Pycnometry of AlSi8Fe9Cr2Ni powders divided by size classes. As size class increases, skeletal density decreases as expected by scientific literature [63].

As illustrated in Figure 4.19, skeletal density decreases as size class increasing. This trend was already descripted in Chapter 3 as function of GA process parameters. Fe\_9 % skeletal density was compared to AlSi10Mg one (commercially CL31). Horizontal dashed lines correspond to theoretical density (or true density) for both compositions. For new composition alloys, true density was assumed as the highest skeletal density measured. While AlSi10Mg was tested just in D < 53  $\mu$ m size class (commercially products were sold already sieved in LPBF dimensional range), Fe\_9 % skeletal density was tested in all size classes. As expected, 20-53  $\mu$ m size

class is relative dense with a very low pores fraction. From this point of view, Fe\_9 % are suitable for LPBF production.

Finally, rheological aspects were evaluated for 20-53  $\mu$ m size class. Hall and Carney funnel tests were performed for flowing behavior evaluation. Tests were conducted as referred in "Analytical Method" Chapter. Both tests failed as common for Al-based LPBF powders. Nonetheless, as mentioned in Chapter 3, AlSi8Fe9Cr2Ni could be considered suitable for LPBF production.

## 4.2.1.2 Single Scan Tracks

SSTs approach was chosen to identify LPBF process parameters. Powders were spread over on AlSi10Mg round platform. SSTs were produced by Concept Laser Mlab Cusing R with parameters listed in Table 22.

SST AlSi8Fe9Cr2Ni							
Conditions	Power	Scan Speed					
Conditions	(W)	(mm/s)					
1		400					
2	85	500					
3		600					
4		400					
5	90	500					
6		600					
7		400					
8	95	500					
9		600					

Table 22: SSTs process parameters used for AlSi8Fe9Cr2Ni alloy processing.

As can be seen in Table 22, 9 conditions were investigated through SSTs approach. P was set between 85-95 W with a step of 5 W while v between 400-600 mm/s with 100 mm/s as step, respectively. These parameters were chosen as intersection between AlSi10Mg SSts parameters [122] and AISI 304L SSTs parameters investigated in Chapter 3. Two repetitions were processed named A and B. As descripted in Chapter 3, automatic algorithm developed in Politecnico was used for the SSTs analysis [122]. Automated selection process results can be observed in Figure 4.20.



Figure 4.20: a) Sample A automated SSTs on-top evaluation results. b) Sample B automated SSTs on-top evaluation results. Results are plotted using Pixel as unit for a comparison between process parameters conditions.

Regularity index, as descripted in Chapter 3, was calculated using Pixel as unit. The algorithm automatically evaluates discontinued SSTs marked them in red. Consequently, red bars mean that SSTs were discontinued. In Fe\_9 % Sample A and B, 85 W parameters (condition 1-2-3) are almost red. For this reason, they were eliminated from massive samples production. Moreover, conditions 2 and 8 (SSTs produced at 500 mm/s) were always evaluated as discontinued and then discarded. Condition 5 were discarded to maintain just the maximum and minimum V obtained by the SSTs investigation and reduced the studied parameters.

Once assessed P-v ranges to study, the size of SSTs was calculated. OL % approach, as descripted by Bosio et al. [127] was applied to calculate H<sub>d</sub> range. Results are visible in Table 23.

Condition	Width [PIXELS]	Width	Hd/OL 5 %	Hd/OL 10 %	Hd/OL 15 %	Hd/OL 20 %
	[]	[µm]	[µm]	[µm]	[µm]	[µm]
4	224	102	97	92	87	82
6	252	115	110	104	98	92
7	200	92	87	82	78	73
9	217	99	94	89	84	79
	Mean	Mean	Mean	Mean	Mean	Mean
	[PIXELS]	[µm]	[µm]	[µm]	[µm]	[µm]
	223	102	97	92	87	81

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Table 23: Evaluation of OL degrees after width calculation for AlSi8Fe9Cr2Ni alloy. Conversion between µm and pixel were calculated using 0.457 values. It derived by magnification degree used during image acquisition.

Hd data in Table 23 are distributed inside 80-95  $\mu$ m range. In addition, 80  $\mu$ m was the reference value obtained by 304L investigation, as exposed in Chapter 3. H<sub>d</sub> parameters were then selected between 80 and 95  $\mu$ m.

For v = 400 mm/s, 80 and 90  $\mu$ m were chosen as H<sub>d</sub>. On the other hand, for v = 600 mm/s, 85 and 95  $\mu$ m were chosen as H<sub>d</sub>. Then, massive samples were produced by Concept Laser Mlab Cusing R.

### 4.2.1.3 Massive samples by LPBF

Fe\_9 % powders were then processed by LPBF technique. Massive samples were built on commercially pure Al platforms. Samples were dimensionally 10x10x4 mm. Lt was kept constant at 15  $\mu$ m value while the other process parameters were listed in Table 24.

Table 24: Massive samples process parameters investigated for AlSi8Fe9Cr2Ni.

Condition	Power	Scan speed	Hatching distance	Layer thickness	VED	
	[ <b>W</b> ]		[ <b>mm</b> ]	[ <b>mm</b> ]	[J/mm <sup>3</sup> ]	
1		400	0.08		187	
2	90	400	0.09	0.015	167	
3	20	600	0.085		118	
4			0.095		105	
5	95	400	0.08	0.015	198	
6		95	400	0.09		176
7			600	0.085		124
8		000	0.095		111	

Building platform was maintained at room temperature because no heating system was provided. Scan pattern was set "Island", as suggested by machine producers. Meander exposure was selected with 1 mm<sup>2</sup> per each island, 1 mm of y-axes shift and rotation of 90° between each layer.

Electro-Discharge Machinig (EDM) technique was performed to remove samples from platforms. Samples were then cut, mounted and polished as described in "Analytical Methods" chapter. OM tests were performed for relative density and microstructure analyses. The complete cross-section of each sample was investigated by 100x images stitching. At least 50 images were used to produce stitched cross-section image. As example, the sample 4 cross-section stitched image can be observed in Figure 4.21.



Figure 4.21: OM stiched image of AlSi8Fe9Cr2Ni sample cross-section.

From cross-section samples images, relative density evaluation was carried out. Images were transformed into binary files and then the relative density was measured. Black pixels were considered sample porosity while white ones were considered sample bulk. Aspect Ratio (AR) was used as shape descriptor to discern between pores and cracks. If AR < 2, black pixels were considered being a pore zone. Otherwise, crack was detected. Relative density takes account of both contributions.



Figure 4.22: Relative density vs. VED plot. Samples are divided in two main groups (A and B) as function of their process parameters.

In Figure 4.22, Relative Density vs VED plots is represented. As can be seen, data are divided in two main groups: A and B. Samples produced with v = 600 mm/s and H<sub>d</sub> equal to 85-95 µm with VED between 100 and 140 J/mm<sup>3</sup> are included in group A. Samples produced with v = 400 mm/s and H<sub>d</sub> equal to 80-90 µm with VED between 160 and 200 J/mm<sup>3</sup> are included in group B. A\_X samples presented a high relative density dispersion while B\_X ones maintained similar relative density values as VED increases. None of the samples reached 98.5 % of relative density.



Figure 4.23: Results of pores and cracks fraction analyses. Cracks were detected as function of their AR (AR > 2)

Moreover, cracks and pores fraction analyses were performed and illustrated in Figure 4.23. B\_X samples displayed cracks fraction always lower than 2.5 % and a limited pores fraction (< 0.6 %). By contrast, A\_X samples showed both higher cracks and pores fractions respect to the B group. By v and H<sub>d</sub> combination, insufficient VED values were reached for a complete densification process. XRD test were then analyzed to understand if phase composition could be affected the solidification process.



Figure 4.24: XRD patterns for 20-53 Fe\_9 % powders, A and B massive samples. As function of cooling rate, different phases appear.

In Figure 4.24 a comparison among XRD patterns obtained from A\_1,B\_3 and 20-53 powdered Fe\_9 % samples. It is immediately evident that several secondary precipitate peaks disappear in LPFB samples. Fe<sub>5</sub>Ni<sub>3</sub>Si<sub>2</sub>, AlNi and Cr<sub>3</sub>Ni<sub>2</sub>Si are not present in A\_sample nor in B one.  $\alpha$ -Al is always the main phase. However, the main peak of this phase in not anymore (1 1 1) at 38,5 ° while a peaks growing in (0 0 2) seems to appear. In addition, it seems that a decreasing VED (and so  $\Delta$ T of solidification) eliminates the (1 1 1)  $\gamma$ -Fe peak at 44.5 ° while 42 ° (0 1 0)  $\epsilon$ -Fe peak is maintained.  $\theta$ -Al<sub>13</sub>Fe<sub>4</sub> still remains the most important among precipitates.



Figure 4.25: Fe\_9 % massive sample SEM analyses; zoom on melt pool boundaries. Comparison between SE and BSD images.

SEM microstructure image is shown in Figure 4.25. As can be seen in Figure 4.25 a, second phases precipitation seems to be prominent just at melt pool border. As confirmation of the dissimilar nature between the phases, in Figure 4.25 b compared the same image acquired by backscattered (BSD) and secondary (SE) electrons detectors. White spots in BSD image confirmed the presence of elements phases with high atomic weights. Unfortunately, no more information could be understood from SEM analyses. Further TEM tests need to be performed.

Vickers hardness tests were performed on Fe\_9% samples. Results were compared to CL31 ones in Figure 4.26.



Figure 4.26: Vickers Hardness as function of relative density for CL31 and  $Fe_9\%$  samples.

Vickers hardness tests results on Fe\_9% are illustrated in Figure 4.26. Higher  $HV_{0.1}$  values were reached by Fe\_9% samples respect to CL31 ones. Fe\_9% hardness mean value is 348.7  $HV_{0.1}$  which is almost 3 times CL31 one (129.9  $HV_{0.1}$ ). Hardness increasing can be associated to an improved solid solution strengthening by Fe, Cr and Ni presence in Fe\_9% chemical composition. In addition, a great amount of intermetallic and precipitate phases were found by XRD analyses (Figure 4.24) which further increased hardness values for precipitation strengthening.

On the other hand, an high standard deviation values are evident from Figure 4.26. This could be associated both to lower relative density and phase homogeneity of Fe\_9% alloy respect to CL31.

# 4.2.2 AlSi8Fe18Cr5Ni3

A second Al-Fe alloy was produced by GA process and then processed by LPBF. In this case, AlSi8Fe18Cr5Ni3 (Fe\_18 %) composition was reached using 1:4 304L to AlSi10Mg weight ratio. The first Al-Fe alloy (Fe\_9 %) developed was set as 9 % wt. Fe in order to be inside the maximum solid solubility range by RSPs (Table 20). The second developed alloy was set beyond that limit. Pre-alloyed powders were characterized by PSD, He-Pycnometry and XRD analyses while microstructure was studied by cross-section inspection with OM, SEM and EDX techniques.

Then, SSTs approach were applied for LPBF process parameters identification as used for Fe\_9 %. Finally, massive samples were produced by Concept Laser Mlab Cusing R and investigated through OM and SEM analyses.

### 4.2.2.1 Powders production and characterization

Pre-alloyed powders were produced by a PSI Hermiga 100 GA plant set in Alessandria site of Politecnico di Torino. In Table 25, used atomization parameters are listed.

Table 25: GA process parameters for AlSi8Fe18Cr5Ni3 powders production.

Composition	AlSi10Mg [Kg]	AISI 304L [Kg]	Atomization Temperature [°C]	Nozzle Diameter [mm]	Top Pressure [barg]	Die Pressure [bar]	Isothermal stage	Post- Atomization Weight [g]	Atomization Yield [%]
AlSi8Fe18Cr5Ni3	1.5	0.45	1200	2.5	0.25	25	1 h / 1000 °C	1692	87

For Fe\_18 % alloy, 1:4 304L to AlSi10Mg weight ratio was used as listed in Table 25. Atomization temperature was set as Fe\_9 % alloy one. In fact, at least 200 °C of superheat ( $\Delta$ T) are guaranteed by ternary isothermal section of Al-Si-Fe phase diagram at 1000 °C (Figure 4.27). Moreover, an isothermal stage of 1 h at 1000 °C was performed. By contrast, at 1000 °C and under vacuum atmosphere, low-melting elements like Mg could be volatilized. Die pressure was decreased respect Fe\_9 % to increase the weight fraction of 20-53 µm size class. In this case, 87 % of atomization yield was reached.



Figure 4.27: 1000 °C isothermal section of Al-Si-Fe ternary phase diagram; adaption from [144]. Red dot represents Fe\_18 % composition inside the phase diagram.

Powders collected in GA main hopper were sieved by Retsch Sieve Shaker AS200 with 20, 53 and 106  $\mu$ m of mesh size. Just the 30 % wt. was collected in 20-53  $\mu$ m.

Even though, more than 500 g were collected which could be considered the minimum quantity for LPBF production, as mentioned in Chapter 3.



Figure 4.28: a) Mass Particle Size Distribution obtained by sieving technique; b) Scanning electron microscopy image of 20-53  $\mu$ m size class of AlSi8Fe18Cr5Ni3 alloy. The image was acquired at 2500x

As could be seen in Figure 4.28.a, the Mass PSD of Fe\_18 % is shifted to the coarse region respect the Fe\_9 % one. 20-53  $\mu$ m is not the main powders size class, while 53-106  $\mu$ m size gains almost 45 %. D > 106  $\mu$ m and D < 20  $\mu$ m sizes both increased of some percentiles their fraction. This coarsening effect on Mass PSD is correctly correlated to a decreasing of die pressure. Notwithstanding, the higher atomization yield compensates a reduction in LPBF size class. In SEM image exposed in Figure 4.28.b), it could be seen a more homogeneous bi-phase structure of powders probably due to Fe, Cr and Ni increasing respect to Fe\_9 % (Figure 4.14.b).



Figure 4.29: OM cross-section analysis of AlSi8Fe18Cr5Ni3 particles in D < 20  $\mu$ m size class. a) particle before etching. b) particle after Keller etching for 8 s.

As can be seen in Figure 4.29a, OM cross-section analysis was performed on D < 20  $\mu$ m size class before etching.  $\alpha$ -Al phase seems to be decreased respect to the Fe\_9 % case (Figure 4.16.a). After etching (Figure 4.29 b) it is evident that a tiny part of particle surface was etched by Keller reagent while the most of the surface is grey-dotted. Only rarely and small white spots (Nano metric phase) survived to the acid attack. In the same way, in Figure 4.30, a similar behavior could be noted after etching of D > 106  $\mu$ m particles.



Figure 4.30: OM cross-section analysis of AlSi8Fe18Cr5Ni3 particles in  $D > 106 \mu m$  size class. a) particle before etching. b) particle after Keller etching for 8 s.

For  $D > 106 \ \mu m$  size class, homogenous bi-phase microstructure is even more evident than  $D < 20 \ \mu m$  one. In Figure 4.30.a, particle cross section shows an almost

complete absence of  $\alpha$ -Al white phase. Concordantly, Figure 4.30.b after etching cross-section illustrates an evident growth of  $\gamma$ -Fe phase. EDX analyses were performed on D > 106  $\mu$ m size class to evaluate the composition of these phases.



Figure 4.31: EDX analyses of  $D > 106 \mu m$  particle. Spots and line EDX were performed for chemical elements identification and quantification.

In Figure 4.31.a, EDX was used to chemically quantify elements on  $D > 106 \mu m$  size class particle. Low atomic weight elements appear darker respect to the high atomic ones. Two point EDX analyses were performed. Point 1 EDX measured elements quantities on lighter phase while point 2 EDX the darker one. Finally, a EDX line was used to compare chemical element presence along the line. As can be seen in Figure 4.31.b, higher quantity of Fe and Cr were detected corresponding to white regions. On the other hand, darker regions seem depleted by heavier elements (Fe, Cr and Ni). In this region, just Al and Si were measured as detailed in Table 26.

Spot	I	Al	]	Fe		Si	(	Cr
	At. %	Wt. %						
1	74.7	64.5	11.1	19.8	10.4	9.3	3.8	6.3
2	95.9	95.8	-	-	4.0	4.2	-	-

Table 26: Results of EDX spots analyses.



Figure 4.32: XRD analyses for AlSi8Fe18Cr5Ni3 alloy and phase variation as increasing particle size.  $\gamma$ -Fe are the most intense peaks for all size class while  $\alpha$ -Al phase increases from 20-53  $\mu$ m size class.

In Figure 4.32 it could be observed the comparison among phase variations as function of size classes for Fe\_18% alloy. As expected by OM analyses, XRD results show similar peaks all across D < 20, 20-53 and D > 106  $\mu$ m size classes.  $\gamma$ -Fe main peak (44,5 °) intensity is equal over size classes respect to Fe\_9 % as confirmation of an increased Fe content. Same trend was detected for  $\epsilon$ -Fe. By contrast,  $\alpha$ -Al main peak (38 °) increases its intensity as particle size increases.  $\theta$ -Al<sub>13</sub>Fe<sub>4</sub> is present in every size classes. Also in this case,  $\theta$ -Al<sub>13</sub>Fe<sub>4</sub> (0 0 3) peak at 22.4 ° is quite intense respect to relative intensity of its XRD reference pattern 98-010-3423. The XRD patterns reflect phases detected in Fe\_9 % case. Once particles morphology microstructure and phase content were assessed, porosity content measurement was performed.



Figure 4.33: He-Pycnometry of AlSi8Fe18Cr5Ni3 powders divided by size classes. As size class increases, skeletal density decreases as expected by scientific literature [63]

As illustrated in Figure 4.33, skeletal density decreases as size class increasing. Fe\_18 % skeletal density was compared to AlSi10Mg one (commercially CL31). Dashed line correspond to theoretical density (or true density) for both compositions. As descripted in Fe\_9 %, true density was assumed as the highest skeletal density measured. 20-53  $\mu$ m size class is relative dense with 0.2 % pores fraction while D > 106  $\mu$ m size class got a pore fraction equal to 0.6 %. In the first case, pore fraction % could be assumed acceptable because is inside the measuring error range. This is not true for D > 106  $\mu$ m size class but it is not used for LPBF production.

Finally, Rheological aspects were evaluated for 20-53 µm size class. Hall and Carney funnel test were performed for flowing behavior evaluation. Tests were conducted as referred in "Analytical Method" Chapter. Both tests failed as common for Al-based LPBF powders. Nonetheless, as mentioned in Chapter 3, AlSi8Fe18Cr5Ni3 could be considered suitable for LPBF production.

#### 4.2.2.2 Single Scan Tracks

SSTs approach was chosen to identify LPBF process parameters as well as Fe\_9 %. Powders were spread over on AlSi10Mg round platform. SSTs parameters are listed in Table 27.

SST AlSi8Fe18Cr5Ni3							
Conditions	Power	Scan Speed					
Conditions	(W)	(mm/s)					
1		400					
2	85	500					
3		600					
4		400					
5	90	500					
6		600					
7		400					
8	95	500					
9		600					

Table 27: SSTs process parameters used for AlSi8Fe18Cr5Ni3 alloy processing.

As can be seen in Table 27, same 9 conditions used for Fe\_9 % were investigated through SSTs approach. P were set between 85-95 W with 5 Was step and v between 400-600 mm/s with 100 mm/s as step, respectively. Two repetitions were processed named A and B and automated selection process results can be observed in Figure 4.34.



Figure 4.34: a) Sample A automated SSTs on-top evaluation results. b) Sample B automated SSTs on-top evaluation results. Results are plotted using Pixel as unit for a comparison between process parameters conditions.

Regularity index was calculated using Pixel as unit. The algorithm automatically evaluates discontinued SSTs marked them in red. Consequently, red bars mean that SSTs were discontinued. In Fe\_18 % Sample A and B, among 85 W parameters, condition 3 was always red. For this reason, they were eliminated from massive samples production. Moreover, condition 1 was once red and so was decided to eliminate from massive production. By contrast, respect to Fe\_9 %, all 90 and 95 W could be possible process parameters. To avoid an high number of samples, it was chosen to investigate the highest and lowest P and v values. In addition, same process parameter used for Fe\_9 % production was also chosen. Same considerations were made on  $H_d$  identification.

#### 4.2.2.3 Massive samples by LPBF

Fe\_18 % powders were then processed by LPBF technique. Massive samples were built on commercially pure Al platforms. Samples were dimensionally 10x10x4 mm. Lt was kept constant at 15  $\mu$ m value. Process parameters were listed in Table 28.

Condition	Power	Scan speed	Hatching distance	Layer thickness	VED	
	[W]	[mm/s]	[mm]	[ <b>m</b> m]	[J/mm <sup>3</sup> ]	
1		400	0.08		187	
2	90	100	0.09		167	
3		600	0.085	0.015	118	
4			0.095		105	
5	95	95	400	0.08	0.015	198
6			100	0.09		176
7			600	0.085		124
8		000	0.095		111	

Table 28: Massive samples process parameters investigated for AlSi8Fe18Cr5Ni3.

Unfortunately, LPBF production was not possible for Fe\_18 % powders. No sample could be built more than 0.5 mm height. Distortions of cube angles and macroscopic cracks were detected during LPBF production as illustrated in Figure 4.35.



Figure 4.35: Fe\_18 % massive samples building platform at job end. Red circled sample was stopped during production. Blue circled sample cracks at the end of production. Green circled sample was analyzed.

In some samples, distortions were so pronounced that their production was stopped to avoid compromising the rest of the job (red circled). Other samples (blue circled) presented cracks macroscopically visible before the platform removing. Finally, remained samples (green circled) were cut off from platform, mounted and polished as descripted in "Analytical methods" chapter. An example of OM micrograph can be observed in Figure 4.36.



Figure 4.36: OM stiched images of AlSi8Fe18Cr5Ni3 sample cross-section.

As can be seen in Figure 4.36, Fe\_18 % massive samples are quite low dense. High delamination occurs between different layers. Moreover, cracks propagate both in longitudinal and transversal directions. Consequently, relative density and pores and cracks analyses were not conducted on Fe\_18 % massive samples. However, polished cross-section was observed by SEM for microstructural investigation.



Figure 4.37: SEM analyses performed on Fe\_18 % massive sample cross-section. In inset a magnification of melt pool border.

In Figure 4.37 both cross-section overview and melt pool border detail were shown. As can be seen, precipitates are distributed all over the section. At melt pool border (zoomed in the inset) precipitates coarsening occurs. On the other hand, at the center of melt pool, precipitates seem to maintain circular or rosette-like shape. EDX analysis was performed on needle-shaped precipitates to understand their chemical composition.



Figure 4.38: line EDX analyses performed on Fe\_18 % melt pool border.

As evident from Figure 4.38, line EDX reveals an increased Fe and Cr content in needle-shaped phase. In addition, Al and Si content slightly decreased obtaining similar results to the powders investigation one (Figure 4.31).

## 4.2.3 AlSi8Fe9Cr2Ni + 5 % vol. TiB<sub>2</sub>

LPBF production issues were found for both Fe\_9 % and Fe\_18 % alloys. As already described in "Al-based new composition alloys" paragraph, several strategies were developed to solve feasibility problems. In our case, chemical composition variation does not affect positively the LPBF feasibility. By contrast, Fe\_18 % is even more difficult to produce by Concept Laser Mlab Cusing R. For this reason, it was chosen to use ceramic particles as inoculant elements inside melt pools. The use of inoculant was initially demonstrated as solution in foundry field and then applied to LPBF [147]. Moreover, it is now commercially developed as standard also for LPBF systems for low weld-able alloys [148,149].

As demonstrated by Martin et al. [143], the inclusion of ceramic particles inside the melt creates an equiaxed grain structure. This is due to the heterogeneous nucleation which starts from ceramic particle surface. In Figure 4.39 the heterogeneous nucleation production strategy is illustrated.



Figure 4.39: LPBF production strategy for increased technology feasibility as proposed by Martin [143].

Fe\_9 % was selected as the most promising chemical composition. For this reason, it was mixed with selected ceramic particles. Titanium di-boride (TiB<sub>2</sub>) was chosen as ceramic inoculant particles. It is one of the most hard ceramic material in nature with excellent mechanical and thermal properties. Its oxidation stability and chemical inertia makes it perfect for metallurgical application. In aluminum industries, it is used as an inoculant to refine the grain size (10x smaller) in aluminum alloys [150] thanks to its high wettability with melts. It is also used as reinforcement in Metal Matrix Composites (MMCs) especially with aluminum matrix. In addition, its presence in MMCs contributes to enhance mechanical properties at high temperatures caused by pinning effects of the reinforcement particles.

#### 4.2.3.1 Powders production and characterization

TiB<sub>2</sub> Grade F powders were provided by H.C. STARCK in 0.5-5  $\mu$ m range. It was mixed in 5 % vol. with AlSi8Fe9Cr2Ni to mitigate hot cracks formation. 5 % vol was chosen for comparison with commercial products [151] and scientific contributions [150,152]. Homogenous dispersion was assured by 24h of mechanical mixing without mixing media.



Figure 4.40: Volume PSD of TiB<sub>2</sub>, Fe\_9% and Fe\_9% + TiB<sub>2</sub>. X-axe is plotted logarithmic for an easier visualization.

TiB<sub>2</sub> Volume PSD were evaluated by Laser Diffraction as descripted in "Analytical methods" chapter. In addition, Volume PSD were performed both for 20-53 Fe\_9 % and 20-53 Fe 9 % + TiB<sub>2</sub> powder. Results are showed in Figure 4.40.

As can be seen, TiB<sub>2</sub> particles mostly present 1-10  $\mu$ m dimension. A small contribution in 0.1-0.5  $\mu$ m is also present so it could be considered as bi-modal powders. By contrast, Fe\_9 % PSD is characterized by a mono-modal Gaussian curve which falls between 10-100  $\mu$ m. Finally, mixed Fe\_9 % + TiB<sub>2</sub> PSD was
evaluated. It is a three-modal curve in which: the first peak is above 5  $\mu$ m and it considered TiB<sub>2</sub> powder contribution. The second peak is above 50  $\mu$ m and it is right shifted respect to Fe\_9 %. This is correlated to the TiB<sub>2</sub> sticky powders on Fe\_9 % bigger particles. Moreover, a third peak is detected above 200  $\mu$ m that could be ascribed to agglomerate formation.

Hall and Carney tests were conducted on Fe\_9 % + TiB<sub>2</sub> powders. However, particles do not flow through the funnel as expected. Finally, He-Pycnometry test was performed. True density of Fe\_9 % + TiB<sub>2</sub> powders were calculated from Fe 9% and TiB<sub>2</sub> ones. Mixture laws were applied as follow:

$$\rho_{Fe_{-}9\%+TiB_{2}} = V_{Fe_{-}9\%} * \rho_{Fe_{-}9\%} + V_{TiB_{2}} * \rho_{TiB_{2}}$$

with  $V_X$  as the fraction volume of Fe\_9% and TiB<sub>2</sub>, respectively. The true density of Fe\_9%+TiB<sub>2</sub> was calculated as 3.12 g/cm<sup>3</sup>. A skeletal density equal to 3.0654 ± 0.0166 was measured. It is higher respect to Fe\_9 % skeletal density but it is lower respect to a 5 % vol. TiB<sub>2</sub> true density. For this reason, 1.8 % of pores could be associated to this difference.

#### 4.2.3.2 Massive samples by LPBF

In Fe\_9 % + TiB<sub>2</sub> massive samples production, SSTs approach was avoided. The Fe\_9 % process parameters were used for comparison with the first part of the work. Fe\_9 % + TiB<sub>2</sub> showed worst flowing behavior during LPBF production respect to Fe\_9 % one. This is consistently with the addition of finer particle fraction and three-modal PSD. Massive samples were built on commercially pure Al platform and extracted by EDM machine. Relative density measurements were performed as descripted in "Analytical methods" chapter.



Figure 4.41: Comparison between Fe\_9 % and Fe\_9 % + TiB<sub>2</sub> Relative density vs. VED plot. All samples increased their relative density.

As detailed in Figure 4.41, both high and low VED samples increase their relative density. This result is mainly ascribed to the  $TiB_2$  inoculant effect. At least 98.8 % of relative density is reached for each sample while some samples present also densities of 99.9 %. From feasibility point of view,  $TiB_2$  addition solves any production issue as expected. Moreover, cracks and pores fractions evaluation was performed.



Figure 4.42: Comparison between Fe\_9 % and Fe\_9 % + TiB<sub>2</sub> pores and cracks fraction plots. All samples decreased their pores and cracks fractions.

As can be observed in Figure 4.42,  $TiB_2$  major effect on solidification process is evident. Both pores and cracks fractions were reduced or eliminated. Pores fraction decreased from 0.1 - 1.1 % to 0.05 - 0.6 %. In the same way, cracks fraction decreased from 1.3 - 3.3 % to 0.05 - 0.9 %. This excellent result was achieved by a uniform dispersion of  $TiB_2$  particles inside massive bulk sample as demonstrated in Figure 4.43. Green circled particles and line EDX indicated the  $TiB_2$  presence both at melt pool center and border.



Figure 4.43: Fe\_9 % + TiB<sub>2</sub> spots and line EDX analyses. Green circled showed TiB<sub>2</sub> presence both in melt pool center and border.



Figure 4.44: XRD analyses for Fe\_9% + TiB\_2 alloy compared to Fe\_9% massive and powders samples .

Finally, XRD analyses were performed on Fe\_9 % + TiB<sub>2</sub> massive sample. Result was compared to Fe\_9 % massive sample and 20-53 Fe\_9 % powder. As shown in Figure 4.44, TiB<sub>2</sub> peaks are evident in black curve. However,  $\gamma$ -Fe, AlNi, Fe<sub>5</sub>Ni<sub>3</sub>Si<sub>2</sub> and Al<sub>19</sub>Cr peaks disappear. Also in this case,  $\alpha$ -Al is always the main phase. In addition, the main peak of this phase in not anymore (1 1 1) at 38,5 ° but (0 0 2) one at 45 °. A reduced content of intermetallic precipitates could be associated to pores and cracks reduction. Further investigation on solidification path need to be performed. Vickers hardness tests were performed on Fe\_9%+TiB<sub>2</sub> samples. Results were compared to CL31 and Fe\_9% ones in Figure 4.45.



Figure 4.45: Vickers Hardness as function of relative density for CL31, Fe\_9% and Fe\_9% + TiB<sub>2</sub> samples.

Fe\_9% + TiB<sub>2</sub> Vickers hardness results are shown in Figure 4.45. Fe\_9% + TiB<sub>2</sub> Vickers analyses were compared with CL31 and Fe\_9% ones. Higher  $HV_{0.1}$  values of Fe\_9% + TiB<sub>2</sub> samples respect to CL31 were detected. However, lower  $HV_{0.1}$  values were measured for Fe\_9% + TiB<sub>2</sub> than Fe\_9%. Fe\_9% + TiB<sub>2</sub> hardness mean value is 304.6  $HV_{0.1}$  with an evident hardness increasing associated to solid solution strengthening by Fe, Cr and Ni as descripted for Fe\_9% alloy. In contrast with

Fe\_9%, a lower amount of intermetallic and precipitate phases were found by XRD analyses (Figure 4.44) in Fe\_9% + TiB<sub>2</sub> alloy. A decreased hardness values can be associated to a lower precipitation strengthening effect.

Similar standard deviation values between Fe\_9% and Fe\_9% + TiB<sub>2</sub> alloy are illustrated in Figure 4.45. In this case, samples phase inhomogeneity could be consistent with this results.

# **Chapter V**

# 5 Conclusions and Further Developments

Additive manufacturing is nowadays considered one of the most promising and advanced manufacturing processes. Laser Powder bed fusion is a mature branch of AM with great potential for short-term industrial switching. Laser Powder Bed Fusion (LPBF) is one of the most industrially developed AM techniques. The Volumetric Energy Density approach is widely used to correlate LPBF process parameters and products' relative density. However, LPBF process parameters are not always fully and adequately investigated. In this thesis, some VED model issues have been discussed. VED was directly correlated with Layer Thickness (Lt), which is rarely debated in the literature. Regarding VED and Lt correlation, some conclusions can be provided:

- Samples produced with  $Lt = 15 \ \mu m$  seem to be unaffected by Scan speed variation.
- At same VED,  $Lt = 15 \mu m$  samples have a higher degree of relative density respect to  $Lt = 30 \mu m$  samples. As consequence, lower VED could be used if Lt is smaller to reach same relative density degree.
- Samples relative density values were compared to literature ones. As the Lt increases (Lt > 30  $\mu$ m), limited relative density values can be reached. Even at high VED values, relative density values close to 99% are not guaranteed.
- VED is confirmed as empirical parameter which is not completely related to densification process, as discuss in Chapter 1. On the contrary, it was confirmed that Lt is strictly correlated to relative density.
- An investigation on VED and Lt influence on Vickers hardness was performed. Results show no correlation among the hardness, VED and Lt. Moreover, there is no evidence of a correlation among VED, Lt and samples phase composition. Both austenitic and ferritic xrd peaks phases maintained constant proportion even if VED was changed.

Lt is not the only LPBF process parameters which was not adequately studied in VED model. Scanning Strategy (SS) can highly influence products final relative density. In fact, at same VED values, a correctly designed SS correctly can improve both relative density leading to shorter production times. Regarding VED and SS correlation, some conclusions can be provided:

- There is a very clear correlation between SS parameters and relative density when VED is kept constant.
- Exposure has a negligible effect on densification process. This trend is appreciable both for stripe no rotation group and stripe rotation 67  $^{\circ}$  group.
- Scan pattern effect is negligible as reported by FM0° and SM0  $^\circ$  results comparison.
- conversely, with previous parameters, Rotation angle between consecutive layers strongly influenced densification process. Relative density of rotated samples reach very high values compared to not rotated ones. The reason could be found in Single-Scan Track geometrical features.
- The introduction of rotations among the layers can reduce porosity presence even at high Hd.
- Moreover, rotation among the layers does not increase production time or cost because is a symmetry operation. Then, 100% relative density can be reached by an Hd optimization (Figure 4.4.e). As explained, all four rotated SS reach 99 % of relative density but from production time point of view, they are very dissimilar.
- The production times as a function of the produced volumes are investigated. The exposure parameter modification could introduce a time saving up to 15 h (Figure 4.5.a). Same results could be noticed also for island scan pattern in Figure 4.5.b)

A Gas Atomization (GA) plant, a PSI Hermiga 100, was fully installed during August 2019. In order to design a new powder composition within our plant, an initial familiarization process was needed, as will be discussed below. AISI 304L was investigated as benchmark product for GA plant validation. Regarding GA plant validation some conclusions can be provided:

5 runs were carried out with AISI 304L. 3 different die pressure were selected: 35 bar was chosen because suggested by PSI staff; on the other hand, 40 and 45 bars were selected to improve the mass yield of powders produced in 20-53 µm range. 20-53 µm range was chosen because it is the one typically adopted in LPBF manufacturing process

- 35 and 40 bars pressure tests were carried out twice for the evaluation of process repeatability.
- The influence of atomization pressure on Dv50 is showed in Figure 3.4, As the pressure increases, the Dv50 decreases as descripted by literature. Runs 1a\*, 1b, 2a and 3 run have similar trend of a 316L powder processed by same GA plant and working conditions [95].
- 20-53 μm fraction yield was considered consistent with literature values [87,88].
- At least 500 g of powders were produced for each run in 20-53  $\mu$ m size class. It is considered enough for a complete characterization and acceptable value for our purpose.

Benchmark powders were characterized to compare them to commercial products. Dimensions and particle size distribution (PSD), physical and chemical features, and finally rheological properties were evaluated. Home-made GA powders were compared to GA commercial powders or to ASTM standards. Regarding the characterization of home-made produced powders, some conclusions can be provided:

- Die pressure was modified to increase LPBF powders production. Run-2a was performed at 40 bar (5 bar more than run-1a\*). A pronounced finerdimension shift of Mass PSD was detected. A reduction of 53-106 µm and an increase of 20-53 µm size classes were obtained.
- Consequently, a further increasing in die pressure was adopted. Run-3 was performed at 45 bar. However, it must be underlined that run-3 atomization was not completed due to an Ar leakage into the atomizer guide tube. For this reason, die pressure was not increased anymore nor run-3 was tested again.
- Runs 1b and 2b were performed to confirm yield mass production. Neither 1b nor 2b confirmed the result obtained during the first trials. However, the lack of particles in the  $D < 20 \ \mu m$  size class for 1a\* and 2b runs was unexpected. These clues could indicate the presence of agglomerates formation of very fine particles. Consequently, agglomerates are trapped in coarser sieves and classified as particles of higher dimensions. Volumetric PSD are then studied to reduce measurement errors.
- Volumetric PSD is purged by artifacts contamination by its technical procedure.

- Run 2b maintain a low  $D < 20 \& 20-53 \mu m$  concentrations, while a very high amount of particles in  $D > 106 \mu m$  size class was recorded. This could be attributed to misleading die pressure value detection.
- In addition, from volumetric PSD data, the effect of die pressure variation seems to vanish. The effect of die pressure variation is not distinguishable trough volumetric PSD. For this reason, numerical PSD was performed.
- Numerical PSD avoids the distortion effects of volume contribution on PSD measuring.
- By Numerical PSD, more than 90 % of particles falls in  $D < 20 \ \mu m$  size class. According to the collected results, 1a\* and 1b runs showed repeatable values. Similar trends were found during 2a and 2b runs. Run-3 owns the higher amount of  $D < 20 \ \mu m$  particles as predicted by literature [61,63]. Fine powder amount is directly correlated to die pressure variation with an acceptable repeatability.
- Focusing on 75-106 and D > 106  $\mu$ m size classes, an unexpected trend was found. As can be seen in Figure 3.8.a, for particle diameters bigger than 75  $\mu$ m, mass and volume distributions do not overlap. The presence hollow powders could be the root reason for these incoherent results.
- The percentage of pores inside particles differs for each size class. For runla\*, a complete cross-sectional Image analyses were carried out. Results are reported in Table 4. Porous powders are frequently produced by the socalled "Bag-crushing" mechanism
- Up to  $D < 75 \ \mu m$  both techniques seem to predicts similarly voids quantification. OM/SEM Image Analyses become more and more inaccurate when applied to Powders with  $D > 75 \ \mu m$  and above.
- He-Pycnometry was performed to evaluate the Skeletal density of the powders for all runs. Percentage of pores could be calculated by the difference between True density of 304L produced by LPBF in literature [98]
- Skeletal density analysis was divided in 3 different zones. There are 3 different trends for all runs. Zone I, i.e. from the finest powders up to class  $53 > D > 63 \mu m$ , zone II, from size class  $53 > D > 63 \mu m$  to  $75 > D > 106 \mu m$  and finally, zone III with particles bigger than 106  $\mu m$ . Skeletal densities vary as function of size class. For all runs, in zone I, density grows slightly. However, in zone II, there is a little decay of the skeletal density. Finally, in zone III, a drop in skeletal density is evident and reported for all runs.
- A probable drop in die pressure could be happened during run-2b, as suggested by He-Pycnometry test, Yield calculation and PSD analyses.
- Among all the morphological parameters, the AR was chosen because it is the simplest shape factor that can be calculated. It is directly correlated to

circularity [99]. In addition, it is the least affected by the magnification used for the measurements.

- GA powders always showed a higher AR than WA powders in accordance with several literature works [61,63,100].
- From a chemical point of view, from run-1a\* to run-2b, all C & S values were acceptable respect to ASTM A240. Run-3 values exceeded standard. For this reason, run-3 was not considered adequate for further analyses. The high concentration of C & S in this run was attributed to a different raw materials composition.
- According to literature a high concentration of N<sub>2</sub> could lead nitrides precipitation. For this reason, N-LECO analyses were performed. No runs exceed the N<sub>2</sub> limits set by standard [96].
- All powders batches showed peaks related to austenite and ferrite phases. According to the model of Cr and Ni equivalents, with the given composition, the delta phase should be inhibited with the exclusive formation of the gamma phase [85] under equilibrium conditions.
- However, cooling rate is strictly related to particle dimensions and phase microstructure. The smaller the particle diameters, the higher the cooling rate becomes. The percentage of delta ferrite decreases with increasing cooling rate. For this reason, it is reasonable to assume that the smaller size fractions are approaching an AF solidification mode whereas the large particles are solidifying as FA. Secondary hopper powders analyses confirmed this assumption.
- Rheological analyses were carried out on powders to evaluate their flow behavior. Rheological characteristics of the different runs are almost identical. There are no variations regardless to the GA conditions.
- GA home-made powders values were also compared with commercial products ones. Both Hoeganas [105] and Sandvick [106] products show similar compact behavior respect to GA home-made powders.
- An almost constant spreadability features from  $1a^*$  to 2b is evident in Figure 3.23. However, run- $1a^*$  is the least spreadable run. This characteristic could be associated to a higher presence of fine powders (D < 10 µm). High CI is associated to a good compaction of powder and so, a poor spreadability. In addition, high AoR values correspond to a high agglomeration tendency. No trend in flowing behavior could be correlated to GA process parameters.
- Furthermore, all runs failed to flow in any funnel (Hall/Carney).
- Finally, Hausner Ratio (HR) was calculated and used to defined flowing behavior class. Also in this case, GA home-made powders products were compared to commercial ones

- HR of produced powders are comparable with Hoeganas [105] and Sandvick [106] ones. Powders move from "Good/free flow" zone to "Passable" zone. Both zones could be acceptable for LPBF production.
- In the end, run-1a\*, 1b, 2a and 2b can be considered suitable for LPBF processes.

Then, influence of GA process parameter on LPBF feasibility was assessed. Single-Scan Track (SST) approach was followed to obtain AISI 304L process parameters starting from 316L once. LPBF process parameters were obtained by SST approach. Regarding the influence of GA process parameter on LPBF feasibility, some conclusions can be provided:

- automated algorithm for on-top shape descriptor for SSTs designed by Marinucci et al. [122]. The on-top width, perimeter length and roughness indexes of the SSTs were evaluated using the algorithm. Algorithm development was necessary to be able to analyze large amounts of data and to obtain values that can be influenced as little as possible by the operator.
- Two process parameters window were investigated. Moreover, powders from run 1a\* and 2b were used to compared results.
- All traces are regular and continuous. Where regularity is not present, the substrate is melted which indicates a lack of powder (spreading problems) rather than a processability issue
- run-1a\* and run-2b were considered identical from feasibility point of view. Consequently, they are defined adequate to LPBF production.
- All runs were then mixed together in order to produce massive cubic samples. So, no influence of GA process parameters was detected in home-made produced powders for LPBF process.

As demonstrated by literature, an increasing number of material have been producing during the last three years. The palette of LPBF material growing day by day. However, the high cost and knowledge need for GA metallic powder production is strongly disincentive. An atomization plant used exclusively for the research and development of materials is the key point of this research. New composition AlSi10Mg-based alloys are pre-alloyed in GA melt chamber and subsequently atomized. Regarding the production of new composition Al alloy, starting from very different melting point raw material, some conclusions can be provided:

- Fe solid solubility in Al is 0.05 wt. % at thermodynamic equilibrium. However, it can be increased up to 12 wt. % using RSPs. For this reason, the first Al-Fe alloy developed was set as 9 % wt. of Fe content. The second developed alloy was set beyond that limit and set as 18%.
- isothermal stage of 1 h at 1000 °C was performed for both alloys. This fact is due to assure the complete melting of 304L in AlSi10Mg melt.
- As expected by ternary isothermal section of Al-Si-Fe phase diagram (Figure 4.13), only liquid phase is presented at 1000 °C.
- By contrast, at 1000 °C and under vacuum atmosphere, low-melting elements like Mg could be volatilized.

Rapid Solidification Processes (RSPs) produce alloys with increased solid solubility of elements in matrix as result of the extreme cooling rates involved in the processes. This new kind of "impossible" (for traditional forming techniques) composition alloys need to be followed by extensive and detailed analyses. Chemical, physical and microstructural characterizations of unstable chemical systems caused by rapid solidification process as GA were performed. Regarding new Al-Fe alloy compositions, some conclusions can be draft:

- In Fe\_18% SEM image exposed in Figure 4.28.b), it could be seen a more homogeneous bi-phase structure of powders probably due to Fe, Cr and Ni increasing respect to Fe\_9 % (Figure 4.14.b).
- This bi-phase structure seems to be quite inhomogeneous for Fe\_9%. For Fe\_9% this inhomogeneity could be detected as particle dimension increases. Keller acid was then used to enhanced this difference as Fe island survived to Keller acid attack. Phase microstructure of powders was studied as function of particle diameter.
- For Fe\_9% alloy, OM particle cross-section analysis was performed on  $D < 20 \ \mu m$  size class before etching. In this OM case, white phase could be associated to Al while dark grey to a Fe phase. After etching (Figure 4.16.b) it is clear that almost all particle surface was etched by Keller reagent. Only rarely and small white spots (nano-metric phase) survived to the acid attack. By contrast, on  $D > 106 \ \mu m$  size class (Figure 4.17), a clear difference could be noted before and after etching. A great amount of Fe island survived to Keller acid attack. This phase seems to be unaffected by acid presence as Fe should be.
- For Fe\_18% alloy, OM particle cross-section analysis was performed on D  $< 20 \ \mu m$  size class before and after etching.  $\alpha$ -Al phase seems to be decreased respect to the Fe\_9 % case. Almost the entire particle shows Fe island survived after etching. Similar features could be noted after etching of D > 106  $\mu m$  particles.

- XRD analyses confirmed the previous findings. γ-Fe main peak phase is less intense respect to other size classes. It confirms a higher relative quantity of α-Al phase in this kind of particles respect to bigger ones. By contrast, α-Al phase do not modify its main peak intensity over the size classes.
- A metastable  $\varepsilon$ -Fe phase was detected at 42 °. It is considered a precursor of  $\alpha$ -martensite phase [146].  $\varepsilon$ -Fe 42 ° peak maintains constant intensity over the size classes.
- A wide range of intermetallic precipitates appears as diameter increased. However, just  $\theta$ -Al13Fe4 seems to be present in every size classes.
- Moreover,  $\theta$ -Al13Fe4 (0 0 3) peak is quite intense respect to relative intensity of its XRD reference pattern 98-010-3423. It could be attributed to a preferential growth caused by LPBF process.
- Skeletal density was tested in all size classes and for all compositions. As expected, 20-53  $\mu$ m size class is relative dense with a very low pores fraction.
- SSTs approach was chosen to identify LPBF process parameters. Once assessed P-v ranges to study, the size of SSTs was calculated. OL % approach, as descripted by Bosio et al. [127] was applied to calculate Hd range.
- Massive cubes samples were produced just for Fe\_9% alloy. For Fe\_18% alloy, no sample could be built more than 0.5 mm height. Distortions of cube angles and macroscopic cracks were detected during LPBF production.
- From massive cubes cross-section samples images, relative density evaluation was carried out. Aspect Ratio (AR) was used as shape descriptor to discern between pores and cracks. If AR < 2, black pixels were considered being a pore zone. Otherwise, crack was detected. Relative density takes account of both contributions.
- In Fe\_9% case, two VED range process parameters were investigated. A\_X samples were produced at low VED values (between 100 and 130 J/mm<sup>3</sup>) while B\_X samples at high VED values (between 160 and 200 J/mm<sup>3</sup>)
- A\_X samples presented a high relative density dispersion while B\_X ones maintained similar relative density values as VED increases. None of the samples reached 98.5 % of relative density.
- B\_X samples displayed cracks fraction always lower than 2.5 % and a limited pores fraction (< 0.6 %). By contrast, A\_X samples showed both higher cracks and pores fractions respect to the B group.
- XRD test were then analyzed to understand if phase composition could be affected the solidification process. For Fe\_9%, several secondary precipitate peaks disappear in LPFB samples. Fe5Ni3Si2, AlNi and Cr3Ni2Si are not present in A\_sample nor in B one. α-Al is always the main phase.

- However, the main peak of  $\alpha$ -Al phase in not anymore (1 1 1) while a peak growing in (0 0 2) seems to appear. In addition, it seems that a decreasing  $\Delta T$  of solidification eliminates the (1 1 1)  $\gamma$ -Fe peak while (0 1 0)  $\epsilon$ -Fe peak is maintained.  $\theta$ -Al13Fe4 still remains the most important among precipitates.
- Using CL31 as reference material, higher HV0.1 values were reached by Fe\_9% samples respect to CL31 ones. Fe\_9% hardness mean value is 348.7 HV0.1 which is almost 3 times CL31 one (129.9 HV0.1).
- Hardness increasing can be associated to an improved solid solution strengthening by Fe, Cr and Ni presence in Fe\_9% chemical composition. In addition, a great amount of intermetallic and precipitate phases were found by XRD analyses (Figure 4.24) which further increased hardness values for precipitation strengthening.

Finally, LPBF feasibility of Fe\_9% was improved using one of the strategy proposed by literature [143]. The inclusion of ceramic particles inside the melt was used to avoid hot-cracks formation. Titanium di-boride (TiB2) was chosen as ceramic inoculant particles. In aluminum industries, it is used as an inoculant to refine the grain size. In addition, its presence in MMCs contributes to enhance mechanical properties at high temperatures caused by pinning effects of the reinforcement particles. Regarding the use of heterogeneous nucleation production strategy, some conclusions can be provided:

- TiB<sub>2</sub> was mixed in 5 % vol. with AlSi8Fe9Cr2Ni to mitigate hot cracks formation. 5 % vol was chosen for comparison with commercial products [151] and scientific contributions [150,152].
- In Fe\_9 % + TiB2 massive samples production, SSTs approach was avoided. The Fe\_9 % process parameters were used for comparison with the first part of the work.
- Fe\_9 % + TiB2 showed worst flowing behavior during LPBF production respect to Fe\_9 % one. This is consistently with the addition of finer particle fraction and three-modal PSD.
- Both high and low VED  $Fe_9\% + TiB_2$  samples increase their relative density respect to  $Fe_9\%$  ones. This result is mainly ascribed to the TiB2 inoculant effect.
- Moreover, cracks and pores fractions evaluation was performed. Both pores and cracks fractions were reduced or eliminated. Pores fraction decreased from 0.1 1.1 % to 0.05 0.6 %. In the same way, cracks fraction decreased from 1.3 3.3 % to 0.05 0.9 %.
- XRD analyses show TiB2 peaks appears in XRD pattern. However,  $\gamma$ -Fe, AlNi, Fe5Ni3Si2 and Al19Cr peaks disappear.

- Also in this case,  $\alpha$ -Al is always the main phase. In addition, the main peak of this phase in not anymore (1 1 1) at 38,5 ° but (0 0 2) one at 45 °.
- A reduced content of intermetallic precipitates could be associated to pores and cracks reduction. Further investigation on solidification path need to be performed.
- Fe\_9% + TiB2 Vickers analyses were compared with CL31 and Fe\_9% ones. Higher HV0.1 values of Fe\_9% + TiB2 samples respect to CL31 were detected. However, lower HV0.1 values were measured for Fe\_9% + TiB2 than Fe\_9%.
- Fe\_9% + TiB2 hardness mean value is 304.6 HV0.1 with an evident hardness increasing associated to solid solution strengthening by Fe, Cr and Ni as descripted for Fe\_9% alloy. In contrast with Fe\_9%, a lower amount of intermetallic and precipitate phases were found by XRD analyses (Figure 4.44) in Fe\_9% + TiB2 alloy. A decreased hardness values can be associated to a lower precipitation strengthening effect.

In summary, new composition Al alloys for AM were developed. The validation of plant and AISI 304L benchmark product demonstrated the comparable feature of homemade products concerning commercial ones. Materials with very different melting temperatures can be atomized without the segregation effect. The extremely high cooling rates of GA allow for the exploration of new ranges of solid solubility for any chemical element. These metastable phases must be deeply investigated as potentially disruptive to material science. However, new composition development needs a robust theoretical method to formulate a rigorous algorithm. In this sense, Artificial Intelligence, Big Data, and Machine Learning applications in material science will grow more and more in the future.

# **Chapter VI**

# **6** Analytical Methods

In this chapter are introduced analytical methods used within the thesis.

### 6.1 Particle Size Distribution

Particle Size Distribution (PSD) is a mathematical function which correlates the size of particle and their frequency of occurrences in a sample. In powders industrial sectors, it is used to estimate the statistical dimension of particles. PSD could be analyzed as distributive function, in which each class is represented by its frequency, or by cumulative one, in which each class is the sum of the previous classes. Some peculiar values of the function are investigated because affect powders properties. These values are easily extracted by cumulative curves.  $D_{10}$ ,  $D_{50}$  and  $D_{90}$  represent the dimension of 10%, the 50% and the 90% of particles, respectively. Other statistical values could be measured to define information, modes and shape of distributive curves. However, them play a marginal role within the additive manufacturing sector.

PSD could be evaluated with 3 different techniques. Each of these techniques obtains a peculiar PSD that provides complementary information between them. PSD could be divided in:

- Mass PSD, obtained through a sieving process as required by ASTM [153];
- Volume PSD, using laser granulometry as required by ISO [154];
- Number PSD, obtained through image analysis of particles for which there is no standard. Notwithstanding, this method is already present in the literature [101].

Mass PSD is the simplest and cheaper way to analyze powders dimension distribution. Particles passed through a series of sieves stacked together. The mesh sizes are smaller and smaller in order to remove coarser particles per each step. At the end of the procedure, sieves were weighted to measure the quantity of powders left on them. In this way, mass of each size class is noted and Mass PSD is calculated. For particles with  $\Phi > 100 \mu m$  or relative dense powders ( $\rho > 4 \text{ g/cm}^3$ ), sieving analyses are really precise and reliable. By contrast, LPBF powders diameter are much more little than 100  $\mu m$ . Therefore, unreliable data could be obtained, especially for smallest size classs. A RETSCH Sieve Shaker AS200 with 20, 32, 45, 53, 63, 75 and 106  $\mu m$  of mesh size were adopted. Sieves were weighted before and after the sieving process in order to obtain the mass fraction of each size class.

Laser granulometry is a technique based on the scattering of a laser with particles. As function of diffraction radius, particles volume was obtained. Fraunhofer or Mie theory were adopted to calculate particles volume. Both theories assume ideal spherical shape for each particle.

A Malvern Mastersizer3000 was adopted for tests. The instrument is composed by an analysis chamber, a hopper and a vacuum cleaner. In the analysis chamber, a laser is diffracted by particles. The diffraction pattern is captured by sensor, set in radial position respect to the beam.

The particles are induced to pass through an analysis chamber by the vibration of the hopper (feeding) and the pressure of the carrier gas (compressed air). For this reason, two parameters could modify particles passage in the analyses chamber; feeding and pressure.

An example of controlling granulometry process parameter is detailed in Figure 6.1. Gas carrier pressure has no effect on PSD. On the contrary, notable influence on PSD is attributed to the feeding of powder (controlled by % of the maximum vibration of the instrument). As the vibration of the hopper decreases, as is evident from Figure 6.1(15% curve), the formation of a secondary peak around 400  $\mu$ m appears and a decrease in the main peak around 55  $\mu$ m occurs. Therefore, the vibration of the hopper influences the test result by disallowing the fine particles to agglomerate.



Figure 6.1: Analyses of Laser Granulometry parameters and effects of feeding and pressure variation.

Moreover, in Volume PSD the frequency of each size class is determined by the total volume of the class. As particle radius become smaller, influence on PSD become lesser and lesser (regression with the cube of the radius). As a consequence, finer particles fraction was greatly underestimated. This distortion is due to the fact of choosing to analyze the curves by volume. In Volume PSD, the weight within the distribution of each particle in its particle size class is influenced by its volume. Given that the volume of the particles is calculated from the cube of their radius, there will be a distortion of the curve due to the fact that the particles with a higher radius will have a predominant volume compared to those with a smaller radius. Using the volume of spheres at a radius of 1, 10 and 100  $\mu$ m, it can be seen how the ratio between volume classes is distorted by the volume of the bigger particles which coincides with the sphere volume equation:

$$V_{Sphere} = \frac{4}{3} * \pi * R^3$$

Size class (Sphere radius) (µm)	Volume * 4.18 (μm³)	Number of particles	Number Fraction (%)	Volume per class * 4.18 (µm <sup>3</sup> )	Volume Fraction (%)
1	1 (10 <sup>°</sup> )	1000 (10 <sup>3</sup> )	91	$1000 (10^{-3})$	0.9
10	1000 (10 <sup>3</sup> )	100 (10 <sup>2</sup> )	9.1	100000 (10 <sup>5</sup> )	9.1
100	1000000 (10 <sup>6</sup> )	1 (10 <sup>°</sup> )	0.9	1000000 (10 <sup>6</sup> )	91

Table 29: Example of influence of bigger sphere volume on particle size distribution in volume for spheres with certain radius.

As detailed in Table 29, the volume per class is highly influenced by the sphere radius rather than the number of particles. Even if there is a particle with a radius of just 100  $\mu$ m, 91 % of volume fraction corresponds to the largest particle size class. To simplify as much as possible, if we consider the case with just 1 particle in 1  $\mu$ m size class and 1 particle in 100  $\mu$ m size class, Figure 6.2 illustrates the enormous difference between Volume and Numerical PSD.



Figure 6.2: Difference between number and volume particle size distribution. Relative % in class changing drastically as plotted above.

Consequently, this implies that it is impossible to evaluate the PSD variation at fine particle sizes if even just one large particle is present. To avoid distortion induced by volume distribution, the number PSD measured by image analysis can be used as an alternative method. Particles images were acquired by Thermofisher Phenom SEM at 500x of magnification. Then, images were analyzed by an automatic algorithm provided by imageJ software.

Number PSD considers each particles as unit. For this reason, volume does not contribute to the distribution calculation. Considering the previous example in Table 29, Number PSD has an opposite trend respect to the Volume PSD. Even the smallest particle contributes as unit in frequency analyses. In case of a large quantities of fine fraction, Number PSD could help to quantify the number per each numerical fraction.

### 6.2 Powder density measurement

Pycnometry is a technique used for volume analyses based on the gas displacement method and the perfect gases law. In this way, relative density of liquids and solid could be easily measured. The foremost popular standard method for powder density measurement is Helium Pycnometry [155]. A He-Pycnometer uses the expansion of He in one or more chambers with a defined volume to calculate samples volume. Then, density is calculated dividing the mass of the sample by its volume. The density, obtained in this way, is defined as skeletal since it considers the pores present within the particles (which therefore its value decreases compared to the Theoretical density). Helium is used as a perfect gas with certain technical limits. It allows for a convenient evaluation of the volume as a function of pressure and temperature through the law of perfect gases.

$$PV = nRT$$

Another possibility for powders relative density measurement is the cross-section of particles and image analyses evaluation. Powders were mounted and polished up to Silica (0.02  $\mu$ m) in order to analyze imperfections and microstructure. Cross-section images are observed and acquired by a Leica DMI 5000 M optical microscope. Captured images were then analyzed using ImageJ, an image analysis software [156].

#### 6.3 Image J

ImageJ is an open-source image analysis software developed by National Institutes of Healt of United States [156]. The software is based on Java and it is based on customable macro and plug-in. It is perfect for image manipulation in order to quantify and measure areas. Algorithms could be developed for any image analyses and stack-operation modes help to automatize folder analyses. In this thesis, ImageJ was used for relative density measurement, both for massive samples and powders. Images binarization is the core of the process. Each image is transform in black and white using adequate threshold values. Threshold values are defined as function of the microscope set during image acquisition. Once black and white images are processed, pixel count measured relative density referring black as pore and white as massive sample. For powders, similar approach was employed.

Finally, ImageJ was also employed for shape evaluation. Shape descriptor, like Aspect Ratio or Circularity, will be used to discern between pores and cracks.

# 6.4 Morphological Test

The study of the shapes of produced particles was carried out using the Malvern Morphologi4 tool which automates the morphological analyses of powders. The instrument is equipped with a Nikon optical microscope coupled to a numerically controlled machine and a powder nebulizer. The powders are sprayed on the test slide through a containment bell. Once deposited, powders are automatically photographed with the chosen lens (varies from 2.5x to 50x) according to the particle size. This process clearly measures contrasted images of the powders and avoids their agglomeration or excessive proximity, which could compromise their morphological properties. There are numerous factors linked to particle shapes, some directly measurable from powder images and others more complex to calculate. In the analysis, it was chosen to cross the results of the evaluation of the particle size (Circle Equivalent Diameter or CED) with their Aspect Ratio (AR). The aspect ratio of each particle was computed by dividing its major axis by the minor axis of the circumscribed ellipse. Based on this definition, the closer the aspect ratio is to unity, the more circular the particle [101]

## 6.5 LECO

The analysis of oxygen, nitrogen and hydrogen is based on inert gas fusion infrared absorption, IGF-IR. The weighted sample is heated up in inert gas atmosphere (mainly helium or argon) in order to melt the material and release the elements of interest. The oxygen present in the sample reacts with graphite crucible to form CO and CO<sub>2</sub>, the hydrogen is oxidized to H<sub>2</sub>O on reactive catalyst. The analytical gases are detected by the system of near infrared cells, NIR, based on the principle that the proper analyte absorbs energy at a specific wavelength. Finally, free nitrogen passes through the thermal conductive detector, TC, that measures the changes of resistance between heated filaments. The concentration content of O, N, H in the sample is calculated according to received analytical signals.

The analysis of carbon and sulphur is performed by combustion analysis and infrared absorption. The weighted sample is place in the furnace in a silica crucible. The furnace is equipped with RF coil to heat the sample and combust it in the stream of oxygen. Carbon and sulphur are oxidized to CO, CO<sub>2</sub> and SO<sub>2</sub>. The gases are swept through the non-dispersive infrared cells on which the signal of SO<sub>2</sub> determines the content of sulphur. The gases pass the active catalyst where CO and SO<sub>2</sub> are oxidized to CO<sub>2</sub> and SO<sub>3</sub>, respectively. Carbon is detected on IR cell as CO<sub>2</sub>. The concentration of analysed sample is normalized according to calibration standards.

# 6.6 Quantometer or Optycal Emission Spectroscopy (OES)

A Quantometer is a direct-reading spectroanalyzer. The instrument is used for the identification and rapid quantitative determination of elements present in a metal alloy sample. For this reason, it is normally diffused as characterization technique in metallography. Intensity of the individual spectral lines and their ratios are measured directly with photoelectric cells placed on the focal surface of the spectrograph. Moreover, all operations are automatic: from the moment the button is pushed which starts the succession of operations, to the reading of the results, the time is about one minute. The reproducibility and precision of the results is equal to that of the best methods of analytical chemistry.

Metal Lab Plus type S7 of GNR srl Analytical Instruments Group is an optical emission spectrometer (Spark-OES) that performs the quality determination of

chemical composition in bulk samples. In principle, in argon atmosphere an electrical spark is applied to the sample that vaporizes a small amount of metal surface and gives unique spectral lines characteristic for particular element thanks to Multi High Resolution CMOS solid state detectors system. The machine may be applicable to different kind of material alloys, ferrous and non-ferrous ones, e.g. Al-, Ni-, Cu-, Mg-, Fe-, Zn-, Ti- based alloys. The concentration results are determined relative to reference materials.

### 6.7 X-Ray Diffractometry

X-Ray diffraction (XRD) analysis was used to characterize phases in the feedstock powders as well as LPBF samples. XRD analysis was carried out on the surface grinded up to 1200 SiC paper by means of a X-pert Philips diffractometer in a Bragg Brentano configuration operated at 40 kV and 40 mA, working with a Cu cathode ray tube ( $\lambda K\alpha 1 = 1.5406$  Å). The analysis was conducted in the 2 $\theta$  range between 10° and 110°, with a step size of 0.013° and 25 s per step. Phase identification was then performed by manual search-match procedure. Powder diffraction file (PDF) reference cards of possible phases were obtained from International Centre for Diffraction data (ICDD) and their peak position and intensity were compared to those observed experimentally.

### 6.8 Apparent, Packing and Tap Density

The Apparent density, Packing density and Tap density tests were developed to evaluate the compaction capacity of powders. This enables the production of dense and compact powder beds and, therefore, increases the relative density of the final product. Apparent density represents the ability of a powder to fill a standard cylinder without the application of stress [157]. Therefore, it measures the density that would be obtained from a cylinder of standard dimensions without further compaction processes. Tapped bulk density is achieved by mechanically tapping a measuring cylinder containing powder. After observing the initial volume, the cylinder is mechanically tapped, and volume readings are taken until the observed change in volume levels off [53]. Packing density is the product between skeletal density and apparent density. As result, it represents the density of a cylinder of standard dimensions without compaction processes with a chosen material.

### 6.9 Funnel Test and Angle of Repose

The ability of a powder to flow is a function of interparticle friction. As interparticle friction increases, flow is slowed. The Hall and Carney flowmeter methods were used to evaluate the flowability of the powder through a funnel while the Angle of Repose (AOR) was used to evaluate the ability of the powders to flow by free-fall on a flat surface. Both Hall and Carney funnel were two different geometries of funnel test which measure flowing time fo 50 g of powder. Some powders, often fine powders, may not flow through the Hall funnel[52]. Nevertheless, if a larger orifice is provided, such as in the Carney funnel[50], a meaningful flow rate may be determined. As already mentioned, these tests have been designed to evaluate the ability of a powder to fill a mold through a hopper. The stress state to which the powder is subjected to is therefore not representative of the stress state during AM processing. Despite this, these results may be useful for comparing the effect of the production process for Gas-Atomization (GA) with respect to commercial powders also produced by GA.

Instead, the Compressibility Index (CI) and the Hausner Ratio (HR) were used to further evaluate the spreadability of the powders through density analysis. HR is the ratio between the tap density and the apparent density. CI is the assessment of the ability of a powder to pack inside a reference geometry. HR and CI is an indication of flow property of powders and is calculated by measuring bulk and tapped density of powders. Based on these values, one can assess whether the powder has good or poor flow (the lower the value of these two parameters, the better the flow) [158]. The Angle of Repose (AOR) represents the steepest angle of descent or dip relative to the horizontal plane to which a material can be piled without slumping. Again, it is a comparative measure of the flow ability of powders.

# 6.10 Metallographic preparation

Powders and massive samples were observed with both optical and scanning electron microscopes. Before observation, metallographic preparation was necessary. Powders samples were mounted in acrylic resin and polished by hand grinding with SiC abrasive papers (up to 4000), with diamond paste (up to 1  $\mu$ m) and then end-polishing the surface with silica oxide suspension (OP-S). For massive samples almost the same procedure was used. Although, no mounting step was necessary in massive samples case.

## 6.11 Optical Microscopy

Samples were observed at Leica DMI 5000 M optical microscope. It is an inverted light optical microscope for metallography. Magnification range varies from 50 to 1000X, bright and dark fields and interference contrast are all at disposal. In order to quantify samples relative density, cubic samples were cut, polished and analyzed at 100X. A minimum of 64 images were analyzed for each sample to check at least 60 mm<sup>2</sup> of samples. Images were then analyzed by ImageJ software as already descripted.

# 6.12 Scanning Electron Microscopy & Energy-Dispersive X-ray

Microstructures of samples were studied by means of Zeiss SupraTM 40 Field Emission Scanning Electron Microscope (FESEM, SEM-FEG Assing SUPRA 25, Zeiss, Jena, Germany) equipped with energy-dispersive X-Ray spectroscopy (EDS) probe. The instrument was equipped with an Oxford Instrument Aztec X-ray system for energy-dispersive X-ray spectroscopy (EDXS) analysis. Thermofisher Phenom SEM was used for powders dimension image analyses.

## 6.13 Vickers Micro-Hardness

Several tests were developed and standardized to measure hardness in metallic materials. A quick, repeatable and accurate test is Vickers Micro-hardness test which measures hardness from the dimension of diagonals of indentation. The required calculations are independent of the size of the indenter. In addition, the indenter can be used for all materials irrespective of hardness. The only precaution is to take in account the minimum distance between indentations and between indentation and sample edges. Minimum distance should be major than 2.5 times diagonal dimension [159].

The micro-hardness testers of the Leica VMHT series provides semi-automatic low-load Vickers hardness testing from 10 g to 1 kg. Using brilliant Leica optics and a high valuable load mechanism with fixed weights to apply the test force, repeatable and longtime stable results are achieved. For AISI 304L samples, Vickers micro-hardness tests were performed on samples keeping the indenter in contact with the surface for 15 s at 0.5 kg of weight.  $HV_{0.5}$  results were obtained. For AISi10Mg and developed composition samples, Vickers micro-hardness tests were performed on samples keeping the indenter in contact with the surface for 15 s at 0.1 kg of weight.  $HV_{0.1}$  results were obtained.

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