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Study of short wavelength laser sources for the additive manufacturing of highly reflective materials

By

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Declaration

I hereby declare that, the contents and organization of this dissertation constitute my own original work and does not compromise in any way the rights of third parties, including those relating to the security of personal data.

Rosa Di Falco

2023

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

Sappiamo bene che ciò che facciamo non è che una goccia nell'oceano. Ma se questa goccia non ci fosse, all'oceano mancherebbe. Importate non è ciò che facciamo, ma quanto amore mettiamo in ciò che facciamo; bisogna fare piccole cose con grande amore.

Madre Teresa di Calcutta

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Abstract

Additive Manufacturing (AM) is assuming an increasingly important role in production thanks to techniques and materials that are taking it out of its traditional role as a tool for rapid prototyping. Although AM hit the headlines around 2000, the introduction of the first stereolithography printers' dates to the 1980s. In any case, the last 10 years have seen such a profound evolution as to allow the application of additive technologies in the manufacturing sector. This evolution has been accompanied by important changes in the management of AM and the birth of new business models: the improvements of the last decade in speed and precision have in fact allowed applications in contexts previously considered uninteresting or unfeasible.

The increasingly complex requests from designers have prompted technologists to increasingly approach the AM revolution. The latter differs from traditional processing technologies because it does not remove material from the raw material but obtains very complex three-dimensional details through the progressive deposit of layers of material.

The Powder Bed Fusion (PBF) process is a laser-based Solid Freeform Fabrication process that uses laser energy to melt a thin layer of metal powder. This process is repeated to produce a three-dimensional metal part and is capable of producing highly complex geometries that are impossible to produce with traditional methods. Compared with traditional manufacturing processes, PBF can also produce parts with higher density. Before a material is machined using this AM process, the suitable machining parameters are first identified. Over the years, various materials have been processed using the PBF process. However, very little has been done on the production of parts in precious metal and in general high-reflective materials such as copper and gold.

This research project is based on two industrial case studies. The first concerns the manufacturing of a combustion chamber for satellite launchers, in the space sector, made by copper alloy. The second case study regards the manufacturing of gold rings, for the jewelry sector. The first steps were the analysis and the assessment of PBF process parameters for copper and gold alloy powders in order to print the components required by the selected case studies. To perform greater absorption for this type of highly reflective materials, has been used a green wavelength laser

source instead of an infrared one. Indeed, it has been proved the better absorption of green laser for the selected materials instead the infrared laser source.

Furthermore, for the second case study, welding tests of gold wires on gold plates were carried out, by using a blue laser source.

Particle size distribution (PSD), bulk density was analyzed for both copper and gold powders before identifying suitable processing parameters for PBF. Due to the high cost and amount of gold material available for this job, a very small build platform was used to optimize material usage and reduce waste. Furthermore, the job was optimized by using the knowledge acquired from the first case study of copper, which appears to have characteristics close to the gold one, but the cost of copper alloys is cheaper than that of gold alloys.

The copper and subsequently the gold cubes were printed by using the appropriate process parameters that were identified first by single-scan melting and after by single-layer experiments. Then the internal porosity of the printed cubes was analyzed. The reached porosity of the cubes was identified to be in the region where process parameters performed a good powder melting. The result was clearly a better material density of the printed components, as well as better mechanical properties and a better surface quality. For copper cubes, the reached average density is 98.7 %. To calculate the roughness, several tests were performed on samples printed with different inclinations. Considering the average roughness calculated, the best case was reached when the inclination angle is 51º. The maximum roughness obtained for gold cubes is 160 µm and the best density is 98.9 %.

Regarding the welding of the gold wires, several tests were carried out by varying the process speed. The best result was found for speeds equal to 3mm/sec.

N.B: Some data are confidential for the companies involved in this thesis, for this reason not all data and parameters can be expressly exposed.

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I would like to extend my gratitude to my Industrial Advisor, Eng. Paolo Calefati, first for his person, for his guidance and encouragement throughout my research. I would also like to thank him for his efforts in helping me organize the work and allow me to complete my PhD on time and above all for being a great teacher. Thanks also to the colleagues who have collaborated with me and thanks to Prima Additive.

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Abbreviations

3DP 3DPrinting

AM Additive Manufacturing

AU Gold

CAD Computer Aided Design

CAM Computer Aided Manufacturing

CFD Computational Fluid Dynamics

CNC Computer Numeric Control

CW Continuous Wave

CU Copper

DED Direct Energy Deposition

DFA Design for Assembly

DFM Design for Manufacture

DFO Design for Orientation

DFAM Design for Additive Manufacturing

DMLF Direct Metal Laser Fabrication

DMLS Direct Metal Laser Sintering

DOE Design of Experiment

FEA Finite Element Analysis

IR InfraRed

LASER Light Amplification by Stimulated Emission of Radiation

LBW Laser beam welding

LC Laser Cladding

LENS Laser Engineered Network Shaping

LW Laser Welding

Nd:YAG Neodymium-doped Yttrium - Aluminum Garnet

PBF Powder Bed Fusion

PSD Particle Size Distribution

RP Rapid Prototyping

SEM Scanning Electron Microscopy

SFF Solid Freeform Fabrication

SLA Stereo lithography

SLM Selective Laser Melting

SLS Selective Laser Sintering

SOA State of Art

UV Ultraviolet

WAAM Wire or Arc Additive Manufacturing

Thesis Outline

Chapter 1 is an introduction to the world of Additive Manufacturing, Laser Welding, the reference market and the objective of this study.

Chapter 2 shows the different laser processes for metal processing, techniques and technologies available in Solid Freeform Fabrication (SFF). The Powder Bed Fusion (PBF) process is explained in detail, including the factors affecting the metalworking as well as the Direct Energy Deposition (DED) process and finally the Laser Welding (LW) process. The reflective materials are then explained with a high focus on copper and gold and the various laser processes.

Chapter 3 describes in detail how the AM process fits into the sectors of our interest, with a focus on the Aerospace and Jewelry sectors. It is also detailed how copper and gold components are printed and the used laser source is described.

In chapter 4 is shown the equipment, used to achieve the objectives of this thesis, the Prima Additive machines are reported in detail, while chapter 5 defines the novelty and the objectives of this research work, the process, and the experimental setup.

Chapter 6 analyzes the results carried out on the samples achieved during the thesis work.

Chapter 7 summarizes the conclusions drawn from this research work and it suggests future work.

Chapter 1

INTRODUCTION

1.1 ADDITIVE MANUFACTURING PROCESS

Additive Manufacturing (AM) is a process in which the manufacture of artifacts takes place by overlapping multiple layers of material starting from a 3D model of the object to be made. The layers are compacted by melting the material which then solidifies in the desired geometry. This process contrasts with subtractive production systems in which material is removed from a solid structure, using techniques such as turning or milling, until the final shape of the object to be produced is achieved. The 3D model from which the process starts can be either the result of a CAD design or the result of a 3D scan of a real object. The software that governs 3D printers divides the digital model of the object into superimposed layers and consequently controls the deposition of the material operated by the printer. The AM process can be carried out with different materials: plastic polymers, metals, and ceramics. Technological evolution has led to the possibility of using materials with industrial characteristics capable of withstanding high temperatures or significant mechanical stress. From the initial use of 3D printing to meet rapid prototyping needs, today AM has come to make it possible to produce parts and components for end use and are particularly suitable in cases where small series productions are made or where great flexibility is needed to satisfy the customization request of a basic product.

Metallic materials are among the most used in the industrial sector. The industry goal is to transform the entire production process with the introduction oof AM systems to replace current production technologies. The limits of metal AM presented in a first phase in terms of production speed and costs, seem to gradually disappear. Thanks to huge investments in research and development at a global level, over the years new technologies and new models of professional AM machines for metals have been developed, more and more performing and accessible. The development of new 3D design software regarding the topological optimization of components has also opened a new concept of design exempt from the design limits dictated by production systems with subtractive technologies. AM also makes it possible to produce on-site components or tools that are needed in departments or workshops.

There are two main process methodologies based on laser technologies, that are used for different scopes and applications:

- ***Powder Bed Fusion (PBF)***
- ***Directed Energy Deposition (DED)***

In both cases the laser is used to melt the metal powders. In the case of PBF processes, the powders are deposited directly on the working area, by creating a bed of powder. A laser beam is directed onto this bed which selectively melts the powder to create the component layer by layer. In the case of DED processes, on the other hand, there is a direct supply of material in the area to be built, whereby the powder is deposited by a nozzle and instantly melted by the laser beam to create the geometry.

AM Advantages

No costs for the construction of plants or for the outsourcing of production processes. Within the new optimized factories based on AM systems, all sectors of the production chain will be hosted: from product design to post-production.

Reduction of the material used, no or minimal waste of raw material thanks to the additive method. In many cases the typical waste of subtractive technologies is drastically reduced, and, in some cases, it is practically nil.

Production speed of metal parts thanks to a direct workflow that passes from the CAD project to the physical model in a few hours and perhaps within the same working environment (thanks to desktop 3D printing systems for metals).

Absence of the geometric constraints dictated by the industrial production of metal parts with subtractive technologies with CNC machines or casting techniques.

On demand production of single pieces, or small-medium volume productions up to industrial scale productions at reduced prices.

New printing innovative materials and the possibility of being able to use, or even mix at the same time, more metals to create new alloys or superalloys to produce components with physical and mechanical characteristics impossible to obtain with traditional production systems.

Greater ease of customization of an object, compared to a basic model, with very low costs to manage the variations. In the same production batch, it is possible to obtain different pieces, made to measure, without the need to intervene on the equipment of the machine.

Reduction of the "time to market" thanks to the possibility of generating small batches to be placed on the market for an initial evaluation of the response of the same, and then intervening with any necessary adjustments that respond to the solicitations collected by the market and only subsequently activate the large-scale production.

Ability to produce what is needed "on site", thus eliminating warehouse stocks and storing "files" - which are launched "on demand" - instead of physical objects.

AM Disadvantages

Limited materials, Additive manufacturing can be limited by the materials available for printing, as not all materials are suitable for the process.

Quality control, Additive manufacturing requires rigorous quality control to ensure that the printed object meets the desired specifications, which can be challenging.

Cost, Additive manufacturing can be more expensive than traditional manufacturing methods, as the equipment and materials required can be expensive.

Size limitations, Additive manufacturing is limited by the size of the print bed, which can limit the size of the object that can be printed.

Environmental impact, Additive manufacturing can have a negative environmental impact, as the materials used for printing may not be recyclable or biodegradable, and the process may require significant energy consumption.

Metal Additive Manufacturing: application sectors

Additive manufacturing for metal components is the most attractive sector industrial application. But what are the sectors that currently use this new additive technology?

Figure 1 shows the different industrial sectors where AM technology is mostly used today.

Aviation and aerospace industry for reasons related to low production volumes, for the high operating cost and last but not least for the possibility of being able to experiment with geometries that are impossible to achieve with subtractive technologies.

Medical and the dental sectors and the surgical sector the first for the level of resolution of the machines and the surgical level due to the possibility of being able to create new ad hoc devices for complex operations.

Automotive and automotive industry at this moment is not very involved in using metal additive manufacturing since the operating cost is still very high compared to conventional manufacturing methods. But automotive is looking for technology solutions that will improve productivity and reliability of this technology.

The world of jewelry that uses printers both for lost wax creations and for direct printing with metal powders.

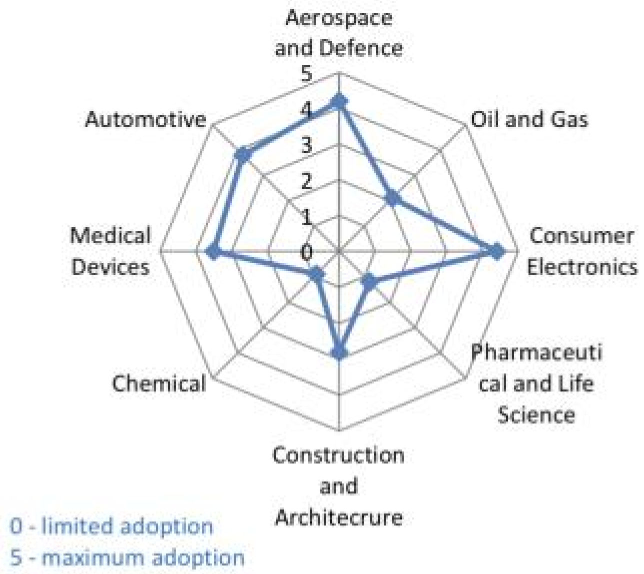

Figure 1: Impact of AM technologies on global industry

1.2 Additive Manufacturing Technologies (AM)

According to ISO/ASTM52921-1 "Standard Terminology for Additive Manufacturing - Coordinate Systems and Test Methodologies", additive technologies are defined as "those processes that aggregate materials in order to create objects starting from their three-dimensional mathematical models, usually by superimposition of layer and proceeding in the opposite way to what happens in subtractive (or chip removal) processes”.

The manufacturing process using additive processes originates from a 3D mathematical model, theoretically definable by means of any three-dimensional CAD. However:

The ability to generate parts with geometries virtually unrelated to "design for manufacturing" constraints allows you to generate "atypical" geometric features for traditional software, such as, for example, trabecular, foam-like, honeycomb structures, etc. that neither traditional design nor most modeling tools can handle efficiently. However, software tools are starting to be available that on the one hand allow you to manage these issues and, on the other hand, to manage the design phases by integrating the definition of geometries with simulation.

The traditional design approaches must be reviewed to exploit the degrees of freedom offered by the new technology, using innovative design approaches that involve the generation of the piece starting from the mission for which it is intended (generative design), opposing the traditional approach that sees a geometry defined by the designer and then verified with calculations and prototypes (real or virtual).

The constraints of the additive process must be considered, with a real "Design for Additive approach" that considers the need to support "cantilevered" parts during construction, the range of materials currently available, the impossibility making holes that are too small, etc.

Always referring to the legislation, the AM can be divided, in principle, according to seven families of processes (Figure 2):

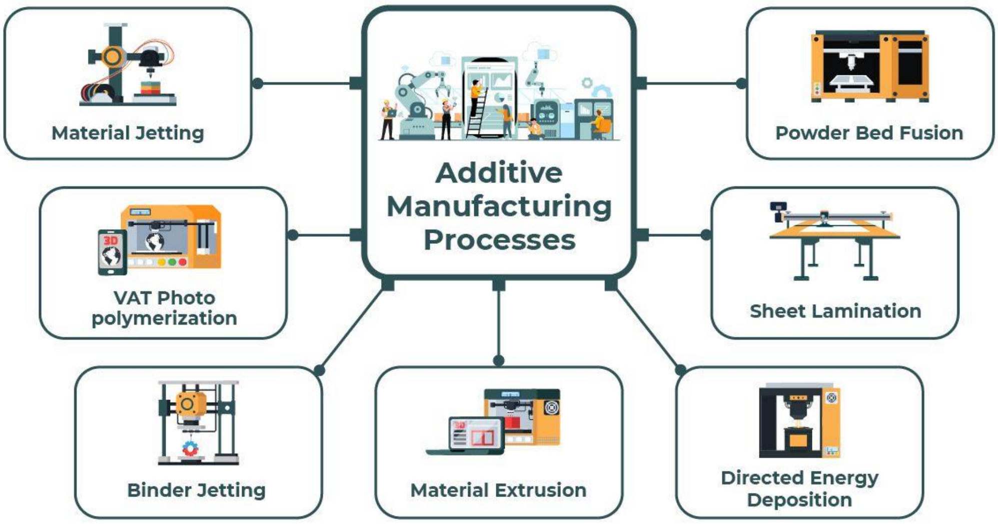

Figure 2: AM Process Family [b]

1. **Material Extrusion,** where the material (usually polymer), brought to the pasty state, is selectively distributed through an orifice; this process is typically the one used in low-cost 3D printing machines.
2. **Material Jetting,** where "droplets" of material are selectively sprayed to create layers (of polymers, wax, or metals).
3. **Binder Jetting,** where a binder in the liquid state is sprayed onto a layer of powder (polymer, ceramic, foundry sand, etc.).
4. **Sheet Lamination,** that creates the product by joining shaped sheets (usually paper but also metal).
5. **VAT Photopolymerization,** based on the selective solidification of a liquid polymer by means of electromagnetic radiation (provided by a laser or similar); the well-known stereolithography process falls into this category.
6. **Power Bed Fusion**, where a suitably concentrated flow of energy, usually supplied by lasers or electron beams, locally melts a layer of powder (metal or polymeric).
7. **Direct Energy Deposition,** where a flow of energy, supplied by a laser, melts the material (typically in the form of metal powder, conveyed to the work area by a special dispenser) when it is deposited to make up the piece.

It is essential to note that the technologies just mentioned must be complemented by a series of fundamental aspects to create a real AM supply chain.

Design for Additive Manufacturing

The numerous advantages of the AM process allow the integration of methods, tools and rules of Design for Assembly (DFA), in order to make the assembly of the product easier and reduce costs. Furthermore, it allows to minimize the number of parts/components to be assembled. The Design for Manufacture (DFM) allows to reduce costs and complexity of the manufactured parts without reducing the quality or performance of the pre-manufactured component. (Benjamin Durakovic, 2018).

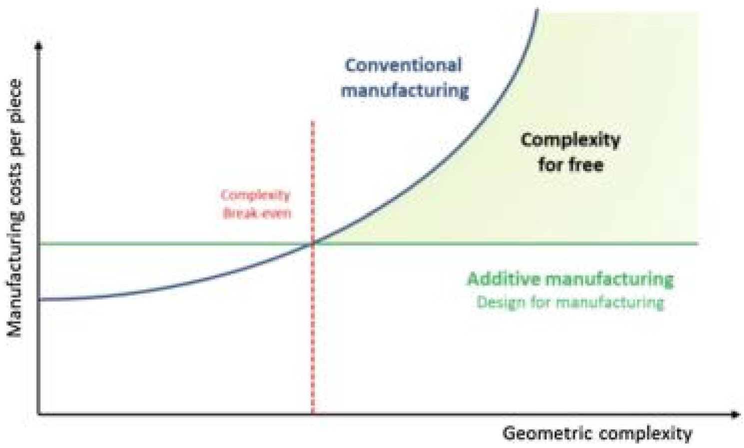

Figure 3: Costs Vs. part complexity for AM technologies

AM technology is known to be expensive and inconvenient to use for trivial geometries. Figure 3, indeed, shows the economic convenience of the AM technology as the geometric complexity of the piece to be molded increases.

The extreme flexibility that the AM process ensures allow also to take advantage from the Design for Orientation (DFO), by which the chosen component can be designed following a chosen printing orientation, in order to optimize, for instance, the maximum height of the building volume and, as a consequence, the amount of powder use and the printing time, or to reduce the number of surfaces to be supported (Figure 4).

These mentioned philosophies are used also for conventional manufacturing, but their integration in the AM context can lead to several benefits:

- Cost and geometry complexity: AM process depends only on production volumes and not on the geometric complexity of the component. Moreover, to achieve desired functionality, numerical simulation helps to place material only where it is required, ensuring weight reduction in aerospace and medical industry applications.

- Functional complexity: moving parts such as bicycle chain, chain mails, armor, crank slider mechanisms, gears, hinge, and various types of joints, can be manufactured directly sing AM (Benjamin Durakovic, 2018).
- Hierarchical complexity: possibility of designing various shapes of internal structure (honeycomb, lattices or foams) to increase strength; properties like weight stiffness and weight ratio can be also improved to reduce material usage and cost.
- Low manufacturing skills.
- Reduced material waste.
- Part and material variety.
- Design method.
- Quality control.

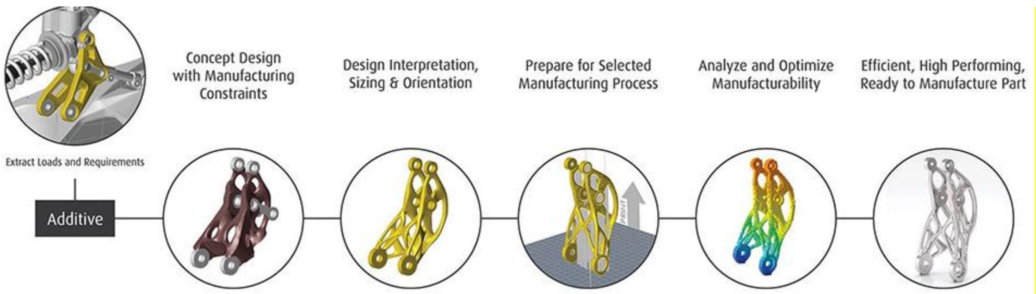

Figure 4: Redesign for AM

The design process aims to take advantage of AM benefits previously mentioned by providing new strategies, tools, techniques, and methods, which can improve manufacturing capabilities.
DfAM methodology follows generally five steps:

- Analysis of the specifications.
- Initial shape.
- Definition of a set of parameters.
- Parametric optimization.
- Validation of the shape.

1.1.1 Powder Bed Fusion

PBF is one of the key direct metal laser sintering (DMLS) processes.

In PBF process, the metal powder is completely melted by means of a laser source, to form a solid part and no further post-processing in the furnace is required. To obtain fully dense and ready-to-use metal parts it is necessary to adjust several process parameters.

The range of commercially available metals for this type of PBF machining is still limited today. This is because the ease of processing varies a lot due to the physical properties of the materials, such as coefficient of thermal expansion, melting point, thermal conductivity, surface tension, laser absorption and viscosity, etc. All metals and metal alloys could be machined into PBF, but this still requires more in-depth study and research.

The typical configuration of a PBF machine is shown in Figure 5.

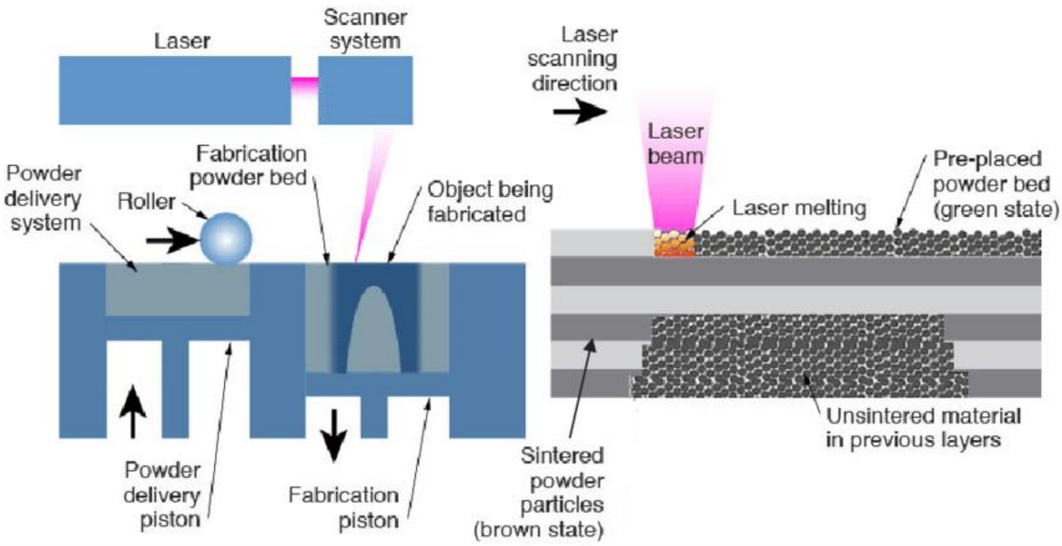

Figure 5: Schematic of the Powder Bed Fusion (PBF) process (Ashraf, 2018).

Generally, this machine consists of three tanks, one which contains the powders for printing, one which contains the piston on which a plate is placed and a third tank for collecting the powders after printing.

The usually very complex parts are built layer by layer on the base plate which is mounted on a piston that moves vertically along the z-axis in the build cylinder. A bin stores the powdered material which is spread over the base plate by various means such as a roller, scraper or a cantilevered hopper. The laser scans the individual cross-sections of the CAD (Computer Aided Design) model layer by layer, thus fusing the powder to create a solid part. The movement of the ram along the z-axis equals the thickness of each slice of the CAD model. The laser component that allows scanning incorporates a system of mirrors to scan at different locations on the baseplate. The F-Theta lens focuses the laser on the point of interest and provides a flat image field along the plane.

The deposition platform is integrated with heating systems that allow the preheating of the powder bed for optimal processing.

When the laser hits the dust particles, the energy is absorbed by them and the laser finally melts the dust to form a solid object, layer by layer. This process is repeated for each section of the CAD model to create a complete 3D object. The process is performed inside an inert chamber to reduce oxidation of the metal.

1.1.2 Selective Laser Melting

SLM is part of the PBF family. This technique melts and fuses metallic powders by using a high power-density laser, which is focused through a system of lenses and mirrors, the schematic process is shown in Figure 6. During the SLM process, the building chamber is always filled with nitrogen gas or argon gas to provide an inert atmosphere to protect the heated metal parts against oxidation and reactive phenomena. Furthermore, some of the SLM machines can provide pre-heating to the substrate plate to ensure a perfect with the first layer of the part and to avoid excessive thermal stresses especially for weak materials. Laser power also ranges between 200 and 1000 W, and its type has a relevant role in the consolidation of powders because its wavelength and energy density influence significantly the powder densification. Together with these parameters, laser power, scanning speed, hatch distance, and layer thickness affect the volumetric energy density that is available to heat up and to melt the powders.

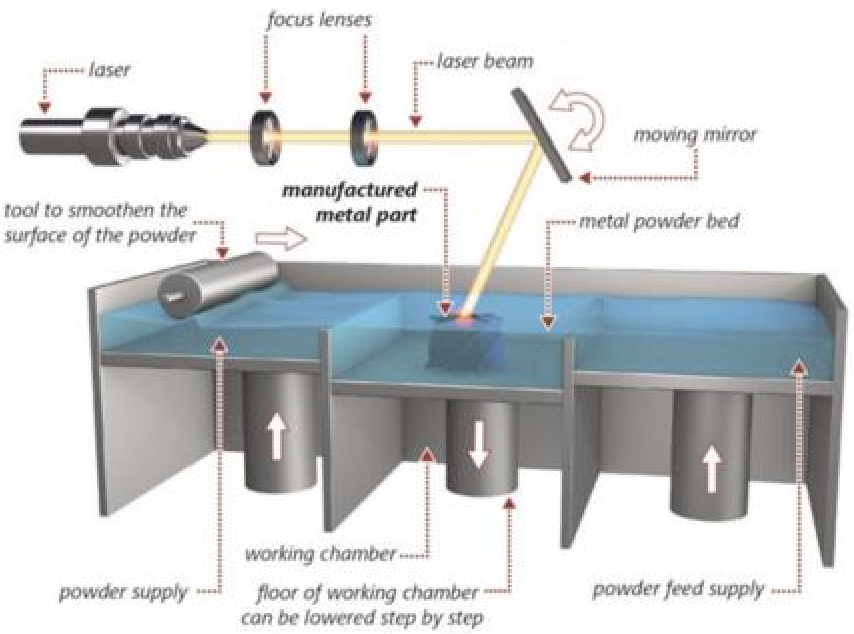

Figure 6: Representation of SLM process

Compared to the conventional manufacturing methods, SLM ensures finer structures in the microstructure at very high cooling rate and, with a well monitored process, the absence of porosity and a material density close to 100 %. Steel, titanium, aluminium and nickel are different types of metals which most of the SLM research revolves around, due to their widespread application and their material cost, but recent research are also focused on other metals such as copper, magnesium and tungsten; however, the commercially available materials are: Aluminium AlSi10Mg, Cobalt Chrome, Maraging Steel, Stainless Steel, Titanium Ti6Al4V and Nickel alloys (Inconel 625 and 718).

1.1.3 Electron Beam Melting (EBM)

Although the EBM process (Figure 7) is similar to the SLM, it differs from it for the thermal source used, which in this case is characterized by an electron beam 472 emitted by a heated tungsten filament, while in the 6547 previous case a laser is used; the electrons generated are collimated and accelerated to a kinetic energy of about 60 keV thanks to two magnetic fields, a focus coil, which is a magnetic lens that focuses the beam to the desired diameter, and a deflection coil, which deflects the focused beam to the desired point on a build platform. The entire process also needs to be done under high vacuum of 10^{-4} to 10^{-5} mbar, as even a small helium gas supply during the melting further reduces the vacuum pressure, allows part cooling and provides beam stability.

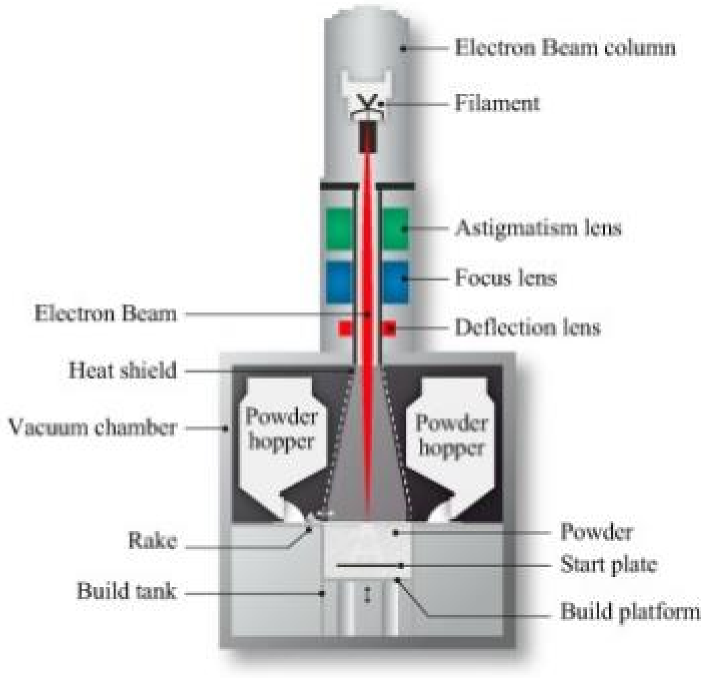

Figure 7: Schematic drawing of an EBM system

The EBM process consists of two different phases (Figure 8):

- Preheating: during this stage a high current beam with a high scanning speed is used to preheat the powder layer to regularize it and to prevent charging of electrons, also known as powder spreading, which can cause build failure during AM process. Previous studies have proven the numerous advantages of preheating, which can increase the effective mechanical strength, electrical, and thermal conductivity of the sintered powder, improving the beam-matter interaction efficiency; it also allows to reduce the formation of balling and to lower the thermal gradient during melting, reducing distortion, warpage, and in-built residual stress (Chu Lun Alex Leung, 2019). On the other hand, this stage increases the overall build time and energy consumption and creates lightly sintered particles that are difficult to remove once the process is finished.

- Melting: this phase is characterized by a low current beam with a low scanning speed which is used to melt the powder; when scanning of one layer is completed, table is lowered, another powder layer is spread and the process is repeated till required component is formed (Bhatwadekar, 2017). The part cross-section is melted in two stages referred to as contouring and hatching. The first improves the surface finish of the part, melts the perimeter of the part cross-section using a constant beam power and speed, and the second, which can follow or precede contouring, performs most of the melting using a beam with variable power and velocity to facilitate the heat dissipation and to prevent overheating. Different hatching strategies have subsequently been developed to improve this process.

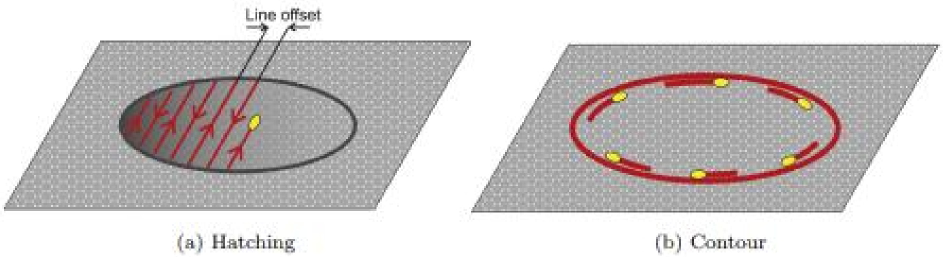

Figure 8: Difference between hatching and contour strategies

Another key factor which strongly affects the EBM process is the powder morphology, which influences preoperties such as powder packing and heat transfer process phenomena (Xibing Gong, 2012). Generally, fine powder with spherical shape is used to ensure high flowability, high build rates and part accuracy; moreover, the material chosen must be necessarily conductive to ensure interaction between the powder and the electron beam, and for this reason the adoption of ceramic materials is virtually impossible. Typical EBM metal powders are Titanium alloys, Cobalt-Chrome and Inconel 718.

Technical specifications of SLM and EBM machines

Table 1 shows the main technical specifications of the SLM and EBM machines.

Table 1: Technical specifications of SLM and EBM machines

	SLM	**EBM**
Power source	One or more fiber lasers of 200 to 1000 W	High power Electron beam of 3000 W
Build chamber environment	Argon or Nitrogen	Vacuum / *He* bleed
Method of powder pre-heating	Platform heating	Preheat scanning
Powder preheating temperature (C)	100-200	700-900
Maximum available build volume (mm)	500 x 350 x 300	350 x 380
Maximum build rate (cm^3/hr)	20-35	80
Layer thickness (μm)	20-100	50-200
Melt pool size (mm)	0.1-0.5	0.2-1.2
Surface finish (Ra)	4-11	25-35
Geometric tolerance (mm)	± 0.05-0.1	± 0.2
Minimum feature size (μm)	40-200	100

1.1.4 Direct Energy Deposition (DED)

When talk about Direct Energy Deposition (Figure 9) we refer to various commercial AM techniques, these include Laser Cladding (LC), Wire or Arc AM (WAAM), and Laser Engineered Network Shaping (LENS).

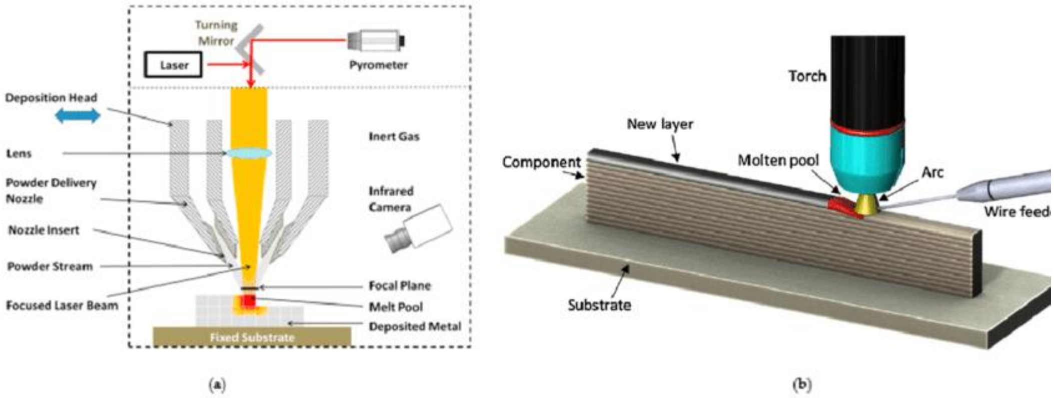

Figure 9: Schematic of DED process (Yusuf, 2019).

These processes make it possible to recreate a three-dimensional metallic component by melting layers of incoming materials, by means of a powder or wire fed nozzle. The wire or powder is directed into the focal point of a high-energy heat source such as a plasma or laser arc typically mounted on a multi-axis arm, which in turn produces a small molten pool in the build area (Matthews, 2018). Thanks to its approach of localized melting and very fast cooling, the resulting microstructure can consist of well-finished grains and has been shown to exhibit 30% higher strength than conventional casting (Gao, 2015).

Unlike the PBF process, DED is mainly used in the repair of worn or damaged metal components, allowing the original part to be rebuilt. DED process is also used for the deposition of coatings on a substrate, to protect or improve the characteristics of the component.

1.3LASER WELDING PROCESS

Laser welding is a process by which it is possible to join two metal components in a single piece, using a laser source that melts the adjacent edges of the two pieces (Figure 10). Welds can be created with or without filler metal.

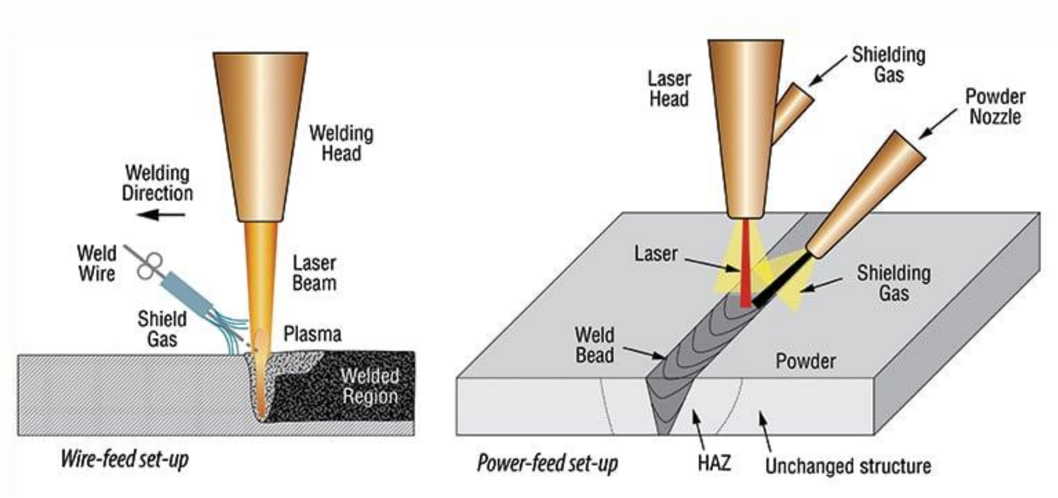

Figure 10: Schematic of the laser welding process

During the welding process, the light emitted by the laser in the form of pulses is absorbed by the material, causing the "keyhole" effect as the beam pierces, melts and vaporizes a part of the metal. When the pulse ends, the molten metal around the "keyhole" begins to solidify again, thus forming a weld spot. A gas is generally used to protect the molten metal.

This type of process has many advantages, in addition to the high process speed there is also a minimum amount of heat added during welding, resulting in a small heat affected area, low part distortion, no slag or spatter and great design flexibility of tools (Czerwinki, 2011).

Laser beam welding (LBW), more commonly referred as laser welding (LW), is a thermal joining technique for bonding metals (and plastics) with the laser. Laser welding is usually a deep penetration keyhole welding technique in engineering applications. The laser beam is focused and aligned to the surface or at a position slightly below the thickness of the material. Due to the extremely high-power density (> 106 W/cm^2) of the focused beam, the metal is vaporized within the keyhole and, as the beam passes along the joint, a surrounding liquefied melt pool flows into the back of the keyhole; the weld pool then solidifies, creating the weld. Laser welding differs from laser cutting in that the molten pool is not blown away by a gas jet: the molten material is instead protected by a low-pressure gas process.

Laser welding uses laser beams that transmit heat to the atoms of the element to be welded. This kind of casting is faster than the others, as it focuses on small surfaces, guaranteeing valuable results. Ideally, for optimal laser welding, the laser beam must be calibrated according to the power and type of material to be processed, this is because, upon contact with the laser, the materials react in different ways.

A lens miniaturizes the laser beam, allowing its energy to be concentrated on a single point. The strong point of laser welding is precisely the possibility of limiting the spectrum of action, with the possibility of increasing and reducing it as needed.

First of all, the welding machine must be set, then the cannula of the laser welding machine must be pointed at the point of intersection of the two bodies, joining them.

Laser welding is particularly suitable for welding jewels, bracelets, and precious metals, resulting very advantageous.

Among the alloys that are most used in the jewelry sector are:

- ***Gold:*** melting point at about 1064 ° C.
- ***Silver:*** melting point at about 961.8 ° C.
- ***Steel:*** melting point at about 1500 ° C.
- ***Aluminum:*** melting point at about 660.3 ° C.
- ***Bronze:*** stable melting at about 1020 ° C.
- ***Copper:*** melting point of about 1085 ° C.

These materials are suitable for laser welding. The laser is a versatile tool, which can be used both in the goldsmith's field and in welding for dental technology, it can be used in the processing of the materials listed above, provided that an assessment is first made of the heat absorption capacity of the materials in question. A second factor to consider is the precision of the laser, whose beam must be conveyed to a single point of the body to be melted, thus hitting a small portion of the surface for a limited period.

Advantages of laser welding for Jewelry

The laser is the ideal method for welding small objects with great care and precision. In fact, laser welding offers several advantages, including:

Versatility, which allows you to enlarge or narrow the portion of the material you want to melt, offering the possibility of treating any type of material.

Effectiveness, the laser guarantees particularly resistant and long-lasting welds.

Safety, which guarantees laser processing without the need to fully heat the bodies, thus avoiding risks associated with burns and scalds.

Speed of reaching the melting point of the materials, possible thanks to the concentration of power on individual parts.

Precision, with no risk of deformation on the machined objects, due to the reduced invasiveness of these machines.

ADDITIVE MANUFACTURING IN AEROSPACE AND JEWELERY

1.4 Additive Manufacturing in Aerospace

In aerospace - whether that's space travel, turboprop, or jet manufacturing - a defect, mismeasurement, or slight error can be the difference between a successful launch and mission failure. It is because of this that aerospace companies have the most stringent requirements for quality and dimensional accuracy.

Manufacturing aerospace parts that have such a high-quality requirement is extremely challenging. With traditional post-machining inspections, many of these parts may have to be completely scrapped or reworked. This scrap and rework can lead to wasted material, production line halts, and supply chain issues for both the OEM (Original Equipment Manufacturer) and connected suppliers. In the end, this will lead to increased cost and delayed programs, results that are unacceptable for any market leader.

One way to greatly alleviate these problems could be to use AM machinery for characteristic parts with complex geometries and even more so for the repair of already existing parts. Reducing the waste of parts that have a very high cost.

Growing penetration of AM in aerospace applications is likely to remain a key factor contributing to the growth of the market. Aircrafts components are normally made using short-run manufacturing and in such cases, AM provides an improvement in production rate. It also helps to produce complex parts, which are lightweight and more resilient compared to products made from traditional techniques. Increasing manufacturing activities in the aerospace and automotive industries in the U.S. is likely to drive the North American market over the coming years.

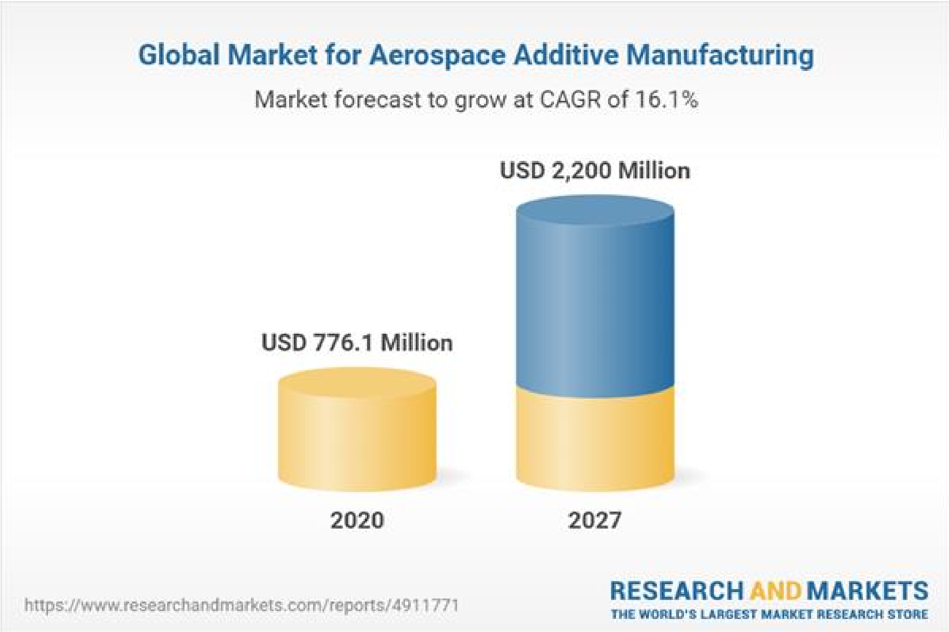

Figure 11: Global Aerospace Additive Manufacturing Market [l]

As reported in Figure 11, despite the crisis due to COVID-19, the global Aerospace Additive Manufacturing market estimated at 776.1 million US Dollars in 2020 is projected to reach a revised size of 2.2 Billion US Dollars by 2027, growing at a CAGR of 16 .1% in the period 2020-2027.

1.5 Additive Manufacturing in Jewelry

The jewelry sector is very complex and with many facets which depend on various factors. Cultural influences play a crucial role in this context, another relevant factor is also the manufacturing method of the jewels. Based on a particular culture, nationality and market, bespoke collections, small series or large series may be more likely. Considering the evident differences between the type of jewel made by a skilled craftsman or an artist, and the jewel produced on a large or even medium scale, the processes and technologies involved differ substantially. Understanding these aspects of the jewelry industry is essential to understand how precious metal AM, primarily based on Laser Beam Powder Bed Fusion (PBF-LB) technology, has challenged the industry to find its niche (Michela Ferraro-Cuda, 2020).

To understand how AM can be a potentially revolutionary technology within this context, it is therefore appropriate to understand how the technical differences of craftsmen and artists can influence the creation processes of the final product which, if until recently was totally entrusted to the expert hands of goldsmiths and their ability to work pieces in precision casting, today it can be prototyped thanks to the massive use of CAD software.

Although the introduction of IT solutions was initially greeted with suspicion and disinterest, linked above all to the goldsmiths' fear of no longer being able to freely express their creative talent, over time the advantages associated with increased productivity, the ability to model shapes and very complex geometries and time and cost savings have slowly created a climate of curiosity and enthusiasm in the jewelry context, especially within the production departments and among product developers.

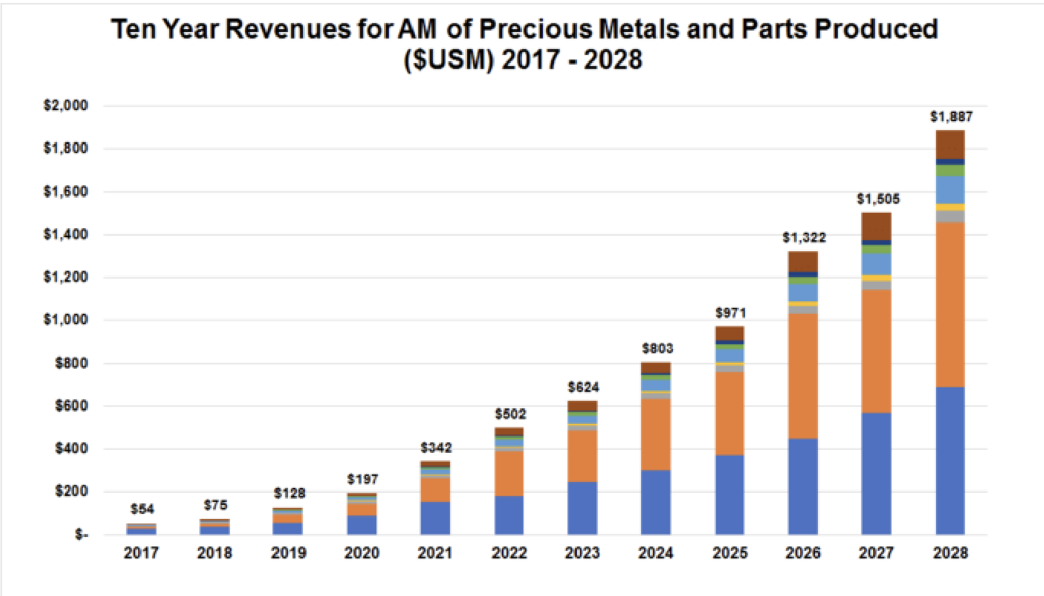

Figure 12: Trend of precious metals use in AM

The first approach chosen to evaluate the quality of the AM production process was to make a comparison with products made with traditional techniques, to understand the actual benefits that this new methodology would bring. Hoping to incur the same benefits that operating, for example, in the aerospace sector, have obtained in terms of weight reduction and number of components that make up an assembly, the jewelry market has however understood that the real advantage of AM results in the production of completely new components. Figure 12, show the trend of precious metals use in AM in the next years.

The key in the jewelry market is therefore to devote oneself to the design, prototyping and production of pieces that have geometries that are impossible to achieve with traditional technologies; this approach would therefore justify an investment that would only be inconvenient and disadvantageous at first glance. The greatest challenge is to envision designs suitable for AM without forgetting the importance of the fundamentals of jewelry design.

As evidence of how AM can be a disruptive technology for this sector, the initial difficulties linked to the limited ability of this technology to produce pieces with very high surface quality are slowly being overcome thanks to the training of highly specialized technicians, the development of parameters extremely effective processes and an ever-increasing understanding of the constraints dictated by the Design for AM.

1.6 Copper and Gold 3D printing

Most research has been focused on the use of a material with reflective and absorbent properties very similar to those belonging of precious alloys: copper. Indeed, the direct study of the behavior of precious metal powders with different granulometry can be inconvenient from the economic point of view, as it would require a considerable investment for the research of the best process parameters.

Figure 13 shows some copper specimens printed using SLM technology.

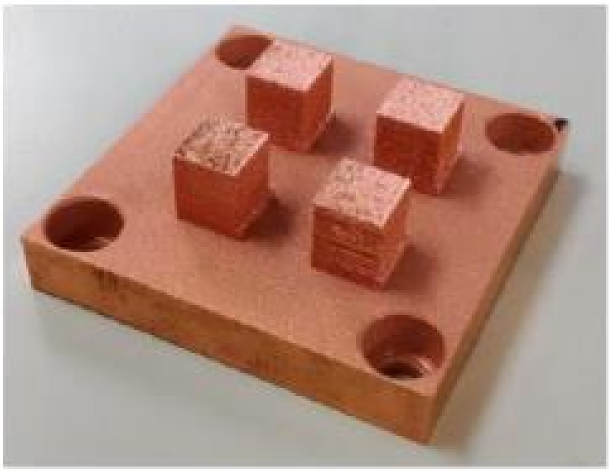

Figure 13: Copper specimens printed with SLM technology.

This material was therefore the main object of study for the evaluation of the interaction with conventional laser sources adopted by the PBF machines, which, working in the infrared, are characterized by a wavelength of 1063 nm. With the aim of making components with relative density higher than 99.5 %, it was immediately realized that, given the low absorbency of the material in these conditions, very high energy densities were required, following the formula for the volumetric energy density:

$$E_v = \frac{P}{v h_d l_t} \tag{7}$$

Where:

- P is the laser power.
- v is the scanning speed.
- h_d is the hatch distance.
- l_t is the layer thickness.

It can be seen how a strong influence is exerted by the power of the laser, which for most of the experiments had to be brought up to 900 W, with very low scanning speeds, of the order of 2-300 mm/s; these parameters are in themselves inconvenient to use, since they require very powerful laser sources of considerable size which, consequently increasing the size of the machines, impact on the amount of material to be used for the process. Finally, the results obtained showed the low tendency of copper to interact with the wavelengths of traditional PBF machines, with a maximum relative density around 97 %, and with energy densities close to 1000 J/mm. Although the surface finish was not in line with what the goldsmith sector requires, settling at about 30-40 microns of Ra, further studies were conducted for the manufacture of pure gold components, however using small-sized machines, primarily to contain the amount of powder used, equipped with IR lasers with very modest powers.

In Figure 14 the cross sections of gold cubes are represented, the (a) is original image (b) is grayscale image (c) is processed image.

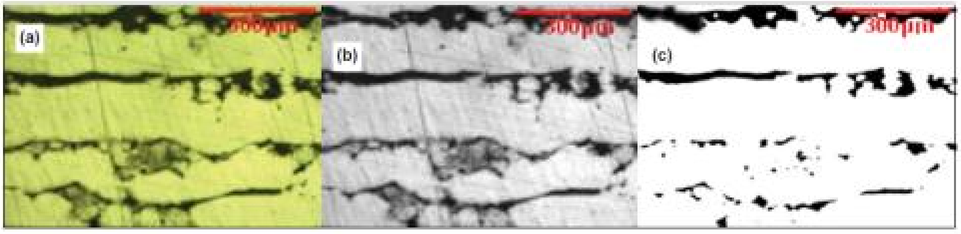

Figure 14: Gold cubes cross section (a) original image (b) grey scale image (c) processed image.

To guarantee the achievement of very high energy densities, using state-of-the-art IR laser technology, very low speeds must therefore be adopted, with the hope of making the material absorb as much energy as possible; however, the most recent research have confirmed the poor workability of gold in such conditions, which make it possible to produce pieces with a maximum density of 90 % in extremely long times.

1.7 Green Laser source for highly reflective materials

What distinguishes the sectors of our interest, Space and above all Jewelry, from all the other sectors of the manufacturing industry is obviously the use of extremely sought-after and expensive materials, which have not only very high procurement costs, but also chemical-physical properties which make them particularly complex to work with additive technologies. All this, combined with the need to obtain high density products with very well finished surfaces for the Jewelry sector, has opened the door to numerous studies which seek to investigate the behavior of precious alloys once subjected to selective laser melting.

Specifically, the particularity of alloys based on gold, silver, platinum and other precious materials lies in the more or less high thermal conductivity and reflectivity, the latter highly difficult to manage when using laser technologies for their manipulation; experimental data show, indeed, that their absorptivity is also linked to the reflective properties of these materials, i.e. the ability to more or less easily absorb the energy supplied by external sources, and which is a function of the wavelength of the beam incident laser. If initially the use of highly reflective alloys had created an unfavorable atmosphere around the use of PBF machines, the continuous demand for new highly performing materials in certain sectors, especially in aerospace and electronics, has pushed towards the study and the use of laser sources of different wavelengths, which could favor the workability of materials that had been very complex to manage until then.

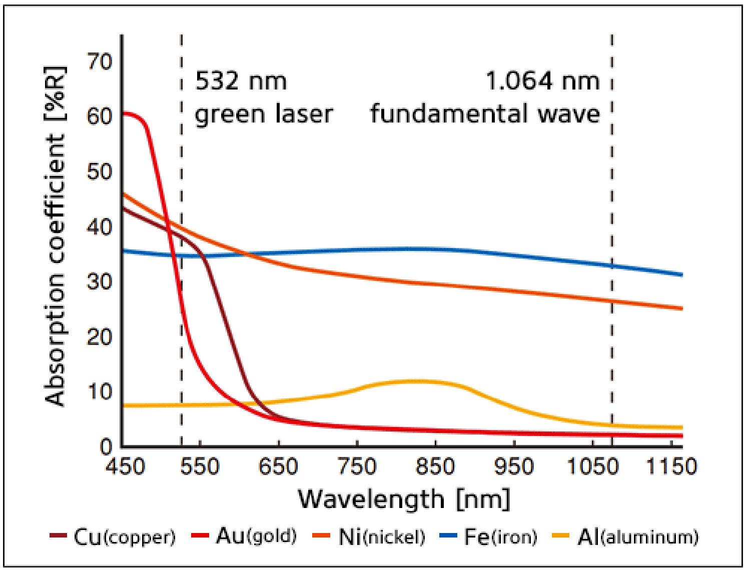

Figure 15: Absorption of highly reflective metals as the wavelength varies [e]

Observing the absorption spectrum of copper (Figure 15), it is evident how the absorptivity of electromagnetic radiation is higher in correspondence of 515 nm than in the IR region; for this reason, the implementation of laser sources of this type, more complex to implement but certainly much more effective has been studied as well. However, there have been few companies that have chosen to include commercial solutions of this type, above all by virtue of the considerable costs deriving from the development of laser and optical systems designed ad hoc for the "green" wavelength, which therefore remained confined for most applications within research centers. In these laboratories the effective advantage of this different solution was demonstrated, which with much lower power, in the order of 200 W, allows to work and produce copper components with much higher density, dimensional tolerances and surface finishes than those obtained in the past. In the following chapter, a study relating to the optimization of the process parameters dedicated to copper and gold will be presented, carried out thanks to the use of a PrintGreen 150, a single laser printer by Prima Additive equipped with a green laser, fiber 200 W Green, 532nm wavelength, QCW, Single Mode.

In Figure 15, it is possible to notice the theoretical benefit in terms of radiation material absorption in additive manufacturing, laser based technology, for high reflective materials such as: Copper, Gold, Aluminum.

- ❑ **Copper.** Green vs IR: +30 times, Blue vs IR: +40 times
- ❑ **Gold**. Green vs IR: +25 times, Blue vs IR: +55 times
- ❑ **Aluminum**. Green vs IR: +3 times, Blue vs IR: +3 times.

Chapter 2

BACKGROUND

2.1 Scope of Research

The new trend of AM in material processing for metal components concerns new materials for the most two interesting sectors: Space and Jewelry respectively for copper alloys and gold/silver. These materials are not threatened by current AM solutions because the traditional IR laser radiation is not absorbed by these materials and the process does not guarantee full material density and good mechanical properties of the printed parts. Especially for Jewelry sector the full density is very important for the surface aesthetic aspect and for the Space field the mechanical properties and the full density of the components are crucial because the printed components are structural parts of satellite launchers.

This research project is focused on exploring the use of short wavelength laser (532 nm green and 450 nm blue) in AM laser-based technology to find solutions for copper and gold alloys, to make the process more efficient and less expensive AM for highly reflective materials. This research will show the benefits that could be achieved by using short wavelength laser sources for copper and gold alloys.

Two industrial case studies are treated for two very relevant sectors. The first case study concerns the production of a copper combustion chamber for satellite launchers, through PBF Additive Production for the Space sector. The second one concerns the production of a gold ring with PBF and the welding of gold threads on gold plates, using a blue laser, for the Jewelry sector.

2.2 SoA

Several studies have been conducted to process materials such as copper and gold through AM, in particular the Selective Laser Melting (SLM) process, i.e., in a powder bed, showing how difficult it is to process this type of materials by using a laser with wavelengths in the infrared (IR) range. These studies (Lykov, 2016), (IMAI, 2020), conducted on copper and (KHAN, 2010) conducted on gold mainly assess the density and microstructure of the molded component.

From the scientific articles mentioned above, some data were extrapolated to show the variation in density as the process speed and the IR laser power used. The data are reported in the following tables, Table 2 shows the density values related to copper, Table 3 shows those related to gold.

Table 2: Density variation for copper processing

Copper Processing - IR state of art		
Power (W)	Speed (mm/s)	Relative Density (%)
750	200	94,5
800	250	95
850	300	95,5
900	350	96
950	400	95,7
1000	450	95,3

Table 3: Density variation for gold processing

Gold Processing - IR state of art		
Power (W)	Speed (mm/s)	Relative density (%)
40	50	84
45	55	84,5
50	60	85
55	65	85,5
60	70	84,7
65	75	84,2

To better understand the trend of the density as the speed and power vary, the data found are reported in the graphs below, respectively for copper (Figure 16) and gold (Figure 17) alloys.

The density of the components is one of the most important characteristics of the material, since the microstructure and therefore the porosity depend on the density, the porosity determines the mechanical characteristics of the final component.

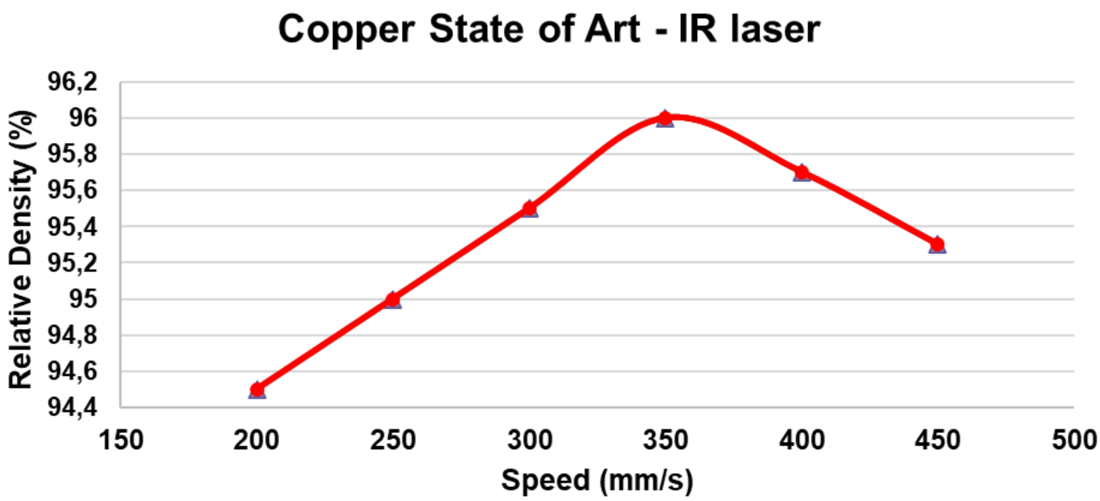

Figure 16: Density trend for copper processing

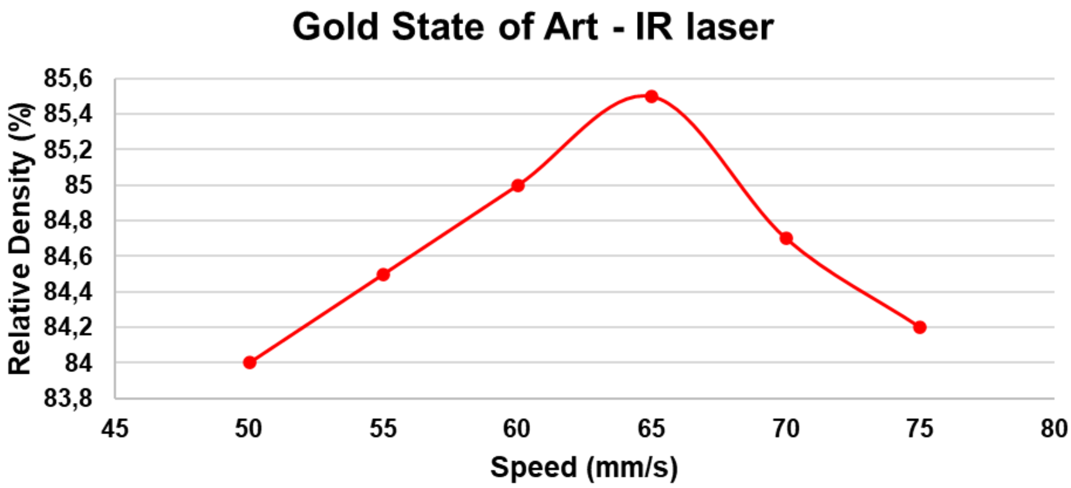

Figure 17: Density trend for gold processing

In Figure 16, it is possible to see how by processing copper with an IR laser the maximum density obtained does not exceed the value of 96 %, for gold in Figure 17, the situation is even worse, the density indeed does not exceed the value of 85,5 %. These low densities determine a high porosity which results in poor mechanical properties of the final component printed in AM.

Another value that certainly should not be overlooked is the low speed used both for copper but above all for gold. Low speed means low productivity and high energy consumption.

For these reasons, in this study the main objective is to improve the density of the printed pieces through additive production, but the possibility of making the process more efficient, making it more productive and therefore obtaining savings from an energy point of view, is not neglected, thanks the use of high efficiency laser sources, with a wavelength more absorbable by copper and gold (Lykoy, 2016; IMAI, 2020; KHAN, 2010).

2.3 Market Trends

The AM market is constantly growing (Figure 18). The potential offered by metal AM is still far from being fully exploited. Technology is constantly evolving, as is the market.

As proof of this, the scenario currently offered by the metal additive market is constantly growing, with significant perspectives.

Market Overview – Metal AM Trend and Forecast

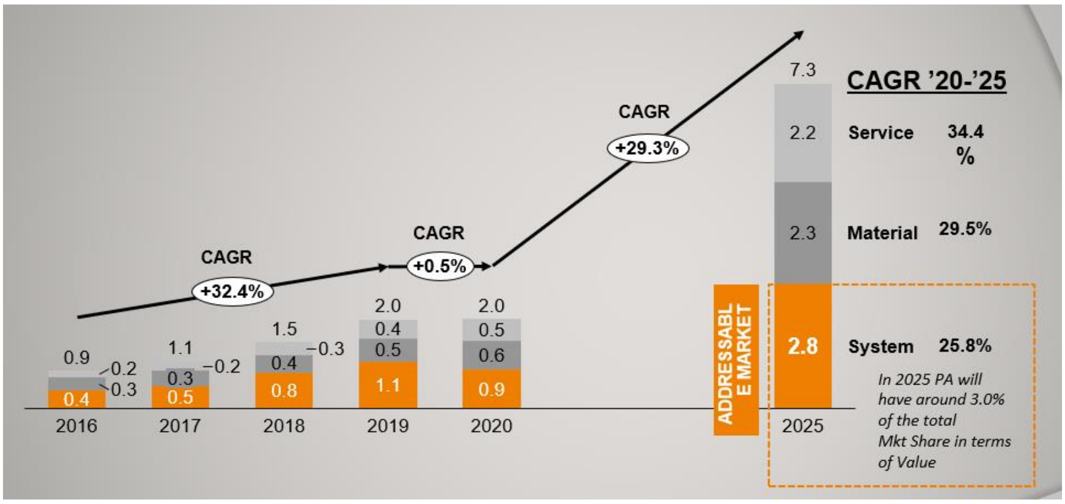

Figure18: Market Overview – Metal AM Trend and Forecast.

In the previous figure is shown the potential growth that is forecasted for the metal AM sectors. The expected growth is calculated to be up to 7.3 B€ in 2025, where 2.2 B€ are related to service (components manufacturing), 2.3 B€ to used materials and 2.8 B€ is regarding the metal AM systems such as those produced by Prima Additive.

The following picture (Figure 19) shows the most interesting sectors in terms of interest and growth for metal additive manufacturing technologies. Aerospace and healthcare are the most attractive sectors in terms of growth. Jewelry is not included because precious materials such as gold and silver, today are not well processed by using infrared laser sources by using metal AM laser-based technologies. One of the scopes of this research is to demonstrate that short wavelength laser could improve growth perspectives in a significant way for AM technology also for the jewelry market.

Market Overview – Metal AM market value by end-markets

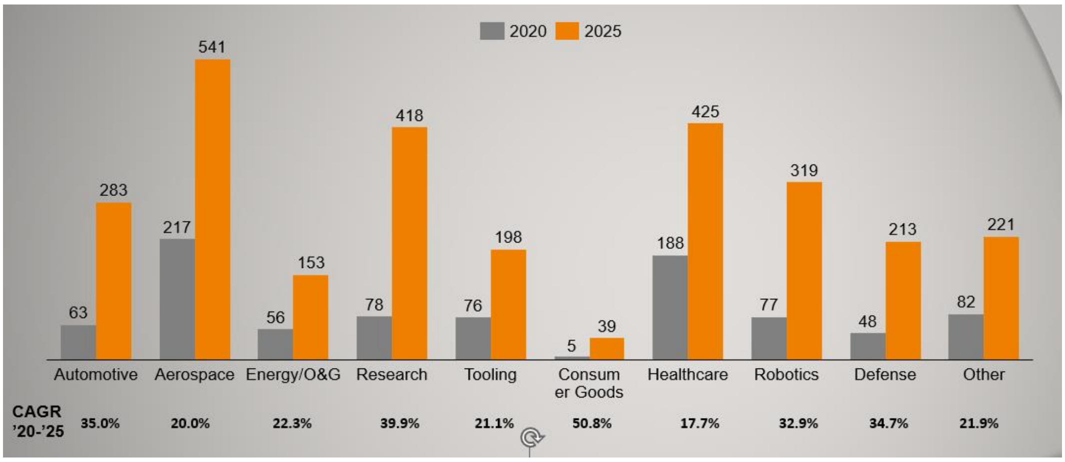

Figure 19: Market Overview – Metal AM market value by end-markets

2.5 High Reflective Metal Materials

In general, metals are known to have high reflectivity, which explains their shiny appearance, indeed when a ray of light encounters a metallic material, the radiation can be absorbed or reflected by the surface.

Since the reflectivity of light by metals is high, their absorption is low because the sum of both must correspond to 100 % of the incident light. Since absorption equals emissivity by Kirchhoff's law (a body emits only as much radiation as it can absorb), this is also low for metals. Absorption of light can occur due to lattice vibrations and excitation of electrons to higher energy levels.

Furthermore, the high reflectance of light in the lower frequencies is associated with the high conductivity of the metal, according to the Hagen-Ruben relationship.

The Hagen–Rubens formula (Equation 1) is a relation between the coefficient of reflection and the conductivity for materials that are good conductors. The relation states that for solids where the contribution of the dielectric constant to the index of refraction is negligible, the reflection coefficient can be written as (in SI Units):

$$R \approx 1 - 2\sqrt{\frac{2\varepsilon_0 w}{\sigma}} \quad (1);$$

where w is the frequency of observation, σ is the conductivity, and ε is the vacuum permittivity.

For metals, this relation holds for frequencies (much) smaller than the Drude relaxation rate, and in this case the otherwise frequency-dependent conductivity σ can be assumed frequency-independent and equal to the dc conductivity . In the infrared region (small frequencies), this equation shows that metals with high reflectance also are good conductors.

Reflection of metallic materials

Due to the high damping constant, which leads to a short distance traveled by light, metals have a high reflectivity, reflecting almost all wavelengths in the visible region of the spectrum.

As shown in Figure 20, some metals have a low refractive index, and according to Snell's law, when light passes through a higher refractive index medium to a low refractive index medium, the refracted ray will have a large deflection from normal.

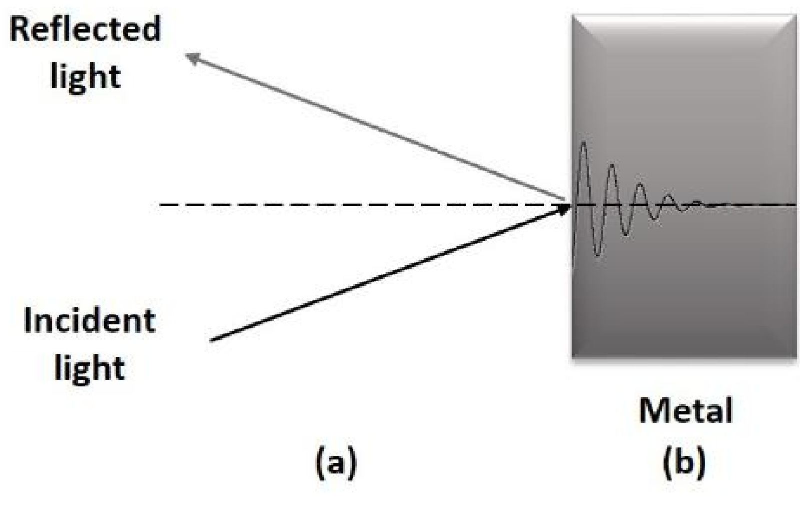

Figure20: Reflectance phenomena where the incidence of light in metal leads to metallic reflection (a) and light attenuation or absorption (b) [c]

The graph of Figure 21 shows the behavior of some metals such as silver, gold, and copper with respect to the incidence of electromagnetic radiation.

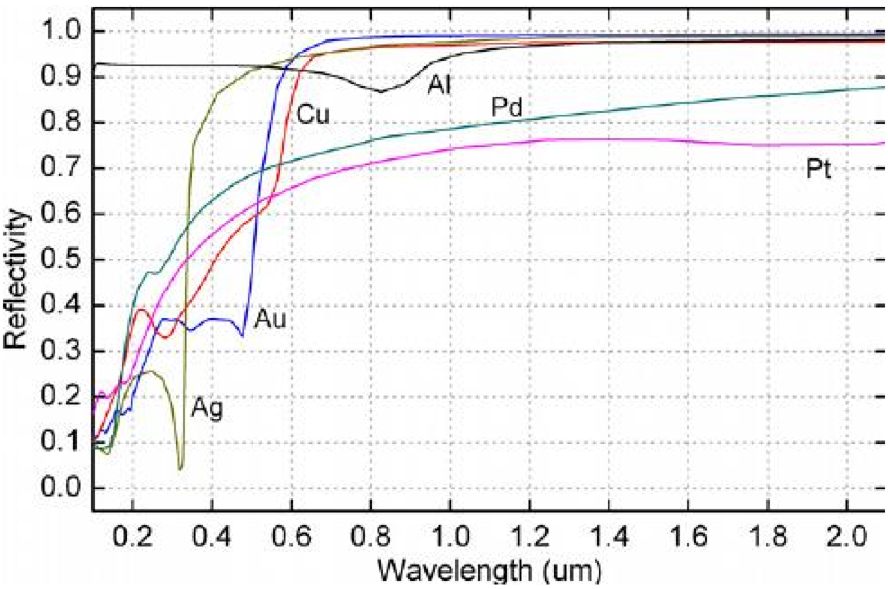

Figure21: Reflectivity of some common metals versus wavelength at normal incidence (Fabian, 2010)

The reflectance spectra of several metals, including gold and copper (materials under consideration for this study) are depicted in Figure 16. Metallic materials can be seen to have high reflectance over a wide range of wavelengths, especially in the visible region of the spectrum. However, if the frequency is high (lower wavelength values), copper and gold exhibit a decrease in reflectance.

The study of metallic reflectance can be applied to metallic coatings, whereby the metal is expected to reflect light in a wide range of wavelengths. Also, it can explain the colors that metals display. Silver, for example, has a high reflectivity in the visible range of the spectrum, rendering it colorless when white light is focused on the metal. Gold, on the other hand, absorbs the blue and violet regions of the spectrum, resulting in a yellow color when illuminated with white light.

Absorption phenomena

In Figure 22 it is possible to see what happens when a ray of light of a certain wavelength is focused on a metal. The radiation is attenuated due to energy loss due to lattice vibrations (heat) and the excitation of electrons from the valence band to the conduction band. In metals, there is an overlap between the valence band and the conduction band or a partially filled valence band, leading to the conduction of electrons at energy levels above the Fermi level.

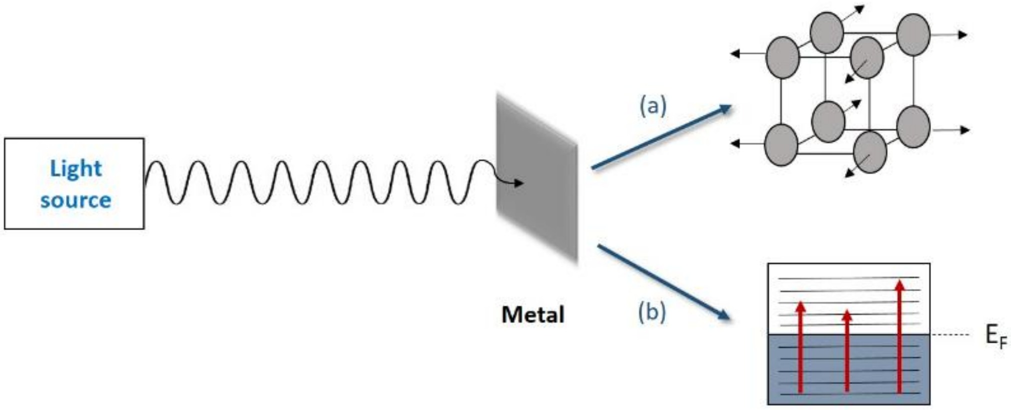

Figure22: Scheme of the absorption of light by a metal, occurring lattice vibrations (a) and electron promotion to higher energy levels (b)

Figure 23 schematizes the process when the electromagnetic radiation meets the metal surface, the intensity of the incident light (I_0) decreases exponentially as it passes through the metal, resulting in a transmitted light (I) of lower intensity.

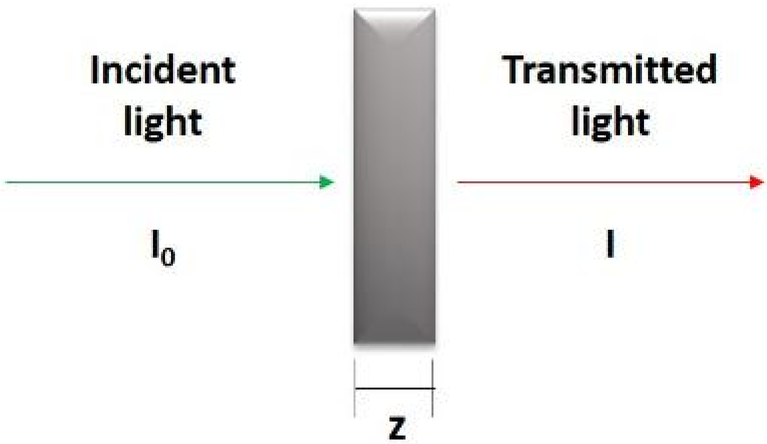

Figure23: Scheme of the initial intensity of light (I_0) changing to transmitted intensity (I) when the radiation passes through a metal with thickness (z)

This happens because metals can dampen the initial light intensity (I_0) and the decrease in light intensity is related to the thickness of the metal (z), the incident wavelength and the damping constant (k) or coefficient of extinction, where k describes the effectiveness of a metal for damping light. This relationship is shown in Equation 2:

$$I = I_0 \, exp\left(\frac{-4\pi kz}{\lambda}\right) \qquad (2);$$

Equation 3 represents the ratio of the transmitted intensity (I) to the initial intensity (I_0) which is defined as the transmittance (T):

$$T = \frac{I}{I_0} \qquad (3);$$

W represents the distance required for the light intensity (I_0) to be reduced by 37% of its initial value. The energy absorbed by the metal as the radiation passes through corresponds to the reciprocal of the penetration depth and is defined as absorbance (α).

The variation of light intensity is related to the penetration depth (W) (Equation 4):

$$w = \frac{1}{\alpha} = \frac{\lambda}{4\pi k} \qquad (4);$$

High-reflection materials have a markedly greater absorption capacity with short wavelengths, while it decreases abruptly in the IR region. This is precisely due to the high reflectivity of the materials.

2.5.1 Copper (Cu)

Copper is a metal with a face-centered cubic crystal structure. It reflects red and orange light and absorbs other frequencies in the visible spectrum due to its band structure, so it has a reddish color. It is malleable, ductile, and an excellent conductor of both heat and electricity. It is softer than zinc and can be polished to a brilliant finish. It is found in group Ib of the periodic table, along with silver and gold. Copper has low chemical reactivity. In humid air it slowly forms a greenish surface film called patina; this coating protects the metal from further attack.

Applications

Most of the copper is used for electrical equipment (60%); construction, such as roofing and plumbing (20%); industrial machinery, such as heat exchangers (15%) and alloys (5%). The main long-standing copper alloys are bronze, brass (a copper-zinc alloy), copper-tin-zinc, which is strong enough to make guns and cannons, and is known as gun metal, copper, and nickel, known as cupronickel, which is the preferred metal for low denomination coins. Copper is ideal for electrical wiring because it is easily worked, can be drawn into fine wires, and has high electrical conductivity.

Table 4 shows the main chemical properties of copper.

Table 2: Chemical properties of copper

Atomic number	29
Atomic mass	63.546 g.mol^{-1}
Electronegativity according to Pauling	1.9
Density	8.9 g.cm^{-3} at 20°C
Melting point	1083 °C
Boiling point	2595 °C
Vandrwaals radius	0.128 nm
Ionic radius	0.096 nm (+1); 0.069 nm (+3)
Isotopes	6
Electronic shell	[Ar] $3d^{10}$ $4s^1$
Energy of first ionization	743.5 kJ.mol^{-1}
Energy of second ionization	1946 kJ.mol^{-1}
Standard potential	+0.522 V (Cu^+/ Cu); + 0.345 V (Cu^{2+}/ Cu)
Discovered	The ancients

2.5.2 Gold (Au)

Gold is yellow metal when in bulk, but when finely divided it can be black, ruby or purple. It is the most malleable and ductile metal; 1 ounce (28 g) of gold can be beaten up to 300 square feet. It is a soft metal and is usually alloyed to give it more strength. It is a good conductor of heat and electricity and is unaffected by air and most reagents. Gold is usually alloyed for jewelry to give it better mechanical properties. The term karat describes the amount of gold present (24 karat is pure gold). It is estimated that all the world gold, so far refined, could be placed in a single cube 60 feet on a side. The most common gold compounds are auric chloride ($AuCl3$) and chloride acid ($HAuCl4$). A mixture of one-part nitric acid to three parts hydrochloric acid is called aqua regia (because it dissolves gold, the king of metals).

Applications

Gold is used as ornament and in jewelry, glass, and electronics. Jewelry consumes around 75% of all gold produced. Gold for jewelry can be given a range of hues depending on the metal with which is alloyed (white, red, blue, green etc.). Colloidal gold is added to glass to color it red or purple, and metallic gold is applied as a thin film on the windows of large building to reflect the heat of the Sun ray. Gold electroplating is used to in the electronic industry to protect their copper components and improve their solderability.

Table 5 shows the main chemical properties of gold.

Table 3: Chemical properties of gold

Atomic number	79
Atomic mass	196.9655 $g.mol^{-1}$
Electronegativity according to Pauling	2.4
Density	19.3 $g.cm^{-3}$ at 20°C
Melting point	1062 °C
Boiling point	2000 °C
Vandrwaals radius	0.144 nm
Ionic radius	0.137 nm (+1)
Isotopes	7
Electronic shell	[Xe] 4^{f14} $5d^{10}$ $6s^{1}$
Energy of first ionization	888 $kJ.mol^{-1}$
Energy of second ionization	1974.6 $kJ.mol^{-1}$
Standard potential	+1,68 V (Au^{+}/Au)
Discovered	c.a. 3000 BC

2.6 Lasers Sources

The term laser is an acronym for “Light Amplification by Stimulated Emission of Radiation”. The solid or gaseous media are stimulated to emit a monochromatic, coherent source of light which is then focused to a point source and delivered to the workplace. A delivery by hard optics explores mirrors and lenses for laser deflection and focusing. A limitation of hard optics is the short distance between the laser source and welded part. The use of fiber optics cable allows for a longer separation of laser source. The latter is also more suitable for manipulation by robotics. There are two major types of lasers, commonly used in industrial applications. The laser of Nd:YAG - Neodymium-doped Yttrium - Aluminum Garnet, explores a crystalline rod and emits light in the ultraviolet range with a wavelength of 1.06 µm. The CO_2 laser is based on gaseous media and has a wavelength of 10.6 µm (Czerwinski, 2011).

Metals are known to have greater reflectivity at wavelengths longer than the incident laser. When a shorter wavelength is used, the metal absorbs more incident radiation, resulting in easier material processing. (Laeng, 2000). For this reason the Nd:YAG laser and the fiber laser which work at similar wavelengths, allow you to process metal more easily than the CO2 laser. According to Kruth, 2003, most metals will have a reflectance of 20-30% relative to the fiber and wavelengths of Nd:YAG lasers.

The absorption of radiation by a metal also depends on several factors such as the type of surface (powder bed or solid surface), the compaction of the powder bed, the type of material and the temperature.

2.7 Factors Affecting the PBF Process

Factors affecting the PBF process can be determined by three main process parameters: material, laser, and environment. This section provides a brief description of these parameters.

2.7.1 Material for Metal processing

PBF solutions use material in the form of a powder.

The absorption of incident radiation by a powder bed is very different from that of bulk metal (Tolochko, 1997).

The percentage of absorption of the incident radiation varies according to the characteristics of the material being processed. Each material has an intrinsic absorption characteristic of the material, for example copper or gold are more reflective than stainless steel, as seen in the previous paragraphs and have a higher absorption for short wavelengths.

Before processing a material, it is necessary to carry out the characterization of the material to verify its physical properties and chemical composition. The physical properties determine the enthalpy of fusion of the metal which is the amount of energy required to completely melt the powder and determines the heat balance. While the chemical composition of a material defines its binding behavior which influences its shrinkage and wettability.

Particle size distribution (PSD)

The PSD (different dimensions) influences the density of the powder bed to be processed. The smaller particles fill all the spaces between the larger particles, creating a more uniform and compact layer that increases the density of the material (Zhu, 2007).

The distribution of the particles also influences the quality of the manufactured component, as a greater quantity of smaller particles reduces the energy required to melt them and improves the surface roughness of the piece (Syvanen, 2000) (Lu, 2001).

If the powder consists of a very high percentage of larger particles, flowability improves but the density of the powder bed is reduced, which may reduce the final density of the part. Therefore, a powder should consist of an adequate number of smaller particles to fill the gaps and increase the density of the powder bed, but not affect the flowability and deposition of the powder.

Absorption

Absorption is the percentage of incident radiation that is absorbed by a material. It is also known as laser/energy coupling. As can be seen from the previous paragraphs, this parameter which depends on the type of material and laser used, is a fundamental parameter.

Particle morphology

The morphology of the powder depends on the method in which it is prepared. In fact, the preparation can take place by grinding, nebulization with water or nebulization with gas. The preparation process determines the shape of the particles and consequently the morphology of the powder.

It was found that the gas atomization technique produces more spherical particles than the other two, and this allows for better powder flowability and better layer and final product quality in AM technologies. While a non-spherical powder has less compaction and therefore the final piece will have greater porosity.

Density

Powder densities can be of two types:

- Density of single particles.
- Packing density.

The density of the individual particles depends on the type of material and is an intrinsic property of the material, while the packing density can be a loose density or a plugged density of the powder depending on the compaction method.

Viscosity

Viscosity is the resistance of the material to flow in the molten state. As a material melts, this characteristic obviously changes as the temperature increases. In fact, a material in the molten state has a higher viscosity which inevitably affects the quality of the finished component.

Specific heat capacity

Specific heat capacity or specific heat is the amount of heat energy required to raise the temperature of a unit amount of material by one degree. The specific heat capacity of the material affects the heat balance.

Latent heat of fusion

The latent heat of fusion is defined as the amount of energy required to change the state of the unit mass of a material from solid to liquid without temperature increase. It is also used in heat balance.

2.7.2 Laser for Metal processing

In a powder bed AM process the properties of the laser beam are of paramount importance. The properties of the laser influence the characteristics of the final component, for this reason it is necessary to set upstream of the process the power of the laser, the size of the spot, the form of pulsed or continuous energy and above all, based on the type of material it is very important choose a certain wavelength, to allow adequate absorption by the material.

Pulsed and continuous wave lasers

There are mainly 2 types of lasers: Pulsed Fiber Lasers and Continuous Wave (CW) Fiber Lasers. While both types of lasers produce light, they differ in how they produce and emit it.

Continuous wave (CW) lasers produce a constant stream of laser light. They are characterized by a constant output power. CW lasers are used in applications that require a stable and constant light output to melt surfaces, such as laser welders and laser cutting machines.

Pulsed lasers, on the other hand, produce bursts of laser light rather than a continuous stream. They feature pulsed power output, resulting in very high peak powers at relatively low average power. This type of laser is used when high peak power is required to ablate contaminants, with a minimum of heat-affected zone on the substrate.

When choosing the laser to be used in an AM process, it is important to remember that various factors influence the absorption of radiation by a material, such as the direction of the incident radiation, the surface roughness, the surface oxides, the wavelength of the radiation incident, material temperature and material type.

2.7.3 Environment for Metal processing

The surrounding working environment also greatly influences the final characteristics of the component.

As already mentioned above, the PBF manufacturing process takes place in an inert chamber to prevent oxidation and the material is spread out on an already preheated platform.

Oxidation is in fact among the least desired phenomena that negatively affect processes involving laser-based metallic materials such as welding, surface treatment and AM. For this reason, it is essential to use a shielding gas during PBF processing, but temperature can also affect the oxidation of the material, according to Rombouts, 2006, the higher the temperature and the superheating of the metal, the greater the oxidation in the molten metals.

The first step in understanding the oxidation of metals and alloys is to address their thermodynamics.

From a thermodynamic point of view, the driving force driving oxidation in a gaseous environment is the Gibbs free energy ΔG, and therefore the spontaneity of the reaction depends on the sign and value of the ΔG. The Gibbs free energy of formation at constant pressure is defined as:

$$\Delta G^0 = -RT\, ln(K) \tag{5}$$

$$\Delta G^0 = \Delta H - T\Delta S^0 \tag{6}$$

where K is the equilibrium constant, ΔH^0 is the enthalpy variation linked to the heat absorbed at constant pressure released during the reaction. ΔS^0 is the change in entropy.

The solution to the oxidation problem in laser metalworking is often an inert environment or shielding gas.

Chapter 3

CHARACTERISTICS OF LASER ADDITIVE SYSTEMS

3.1 Prima Additive

Prima Additive S.r.l is part of the Prima Industrie S.p.A Group, founded in 1977 and listed on the Italian Stock Exchange since October 1999. For over 40 years it has been designing, manufacturing, and marketing high-power systems for cutting, welding and treating three-dimensional components (3D) and planes (2D), panel benders and benders, additive manufacturing systems. Prima Industrie has production plants in Italy, Finland, USA, and China, with a total of about 1800 employees. Now on the market for over 4 decades, it boasts over 14,000 machine installations in more than 80 countries.

One of the most significant events for Prima Industrie was the launch of the new Prima Additive division, during the Innovation Day on 3 October 2018. The new division of the company was created with completely new spaces located at the headquarters of the group in Collegno (TO).

Prima Additive was born from the merger of 3DnT innovative start-up founded in 2015 and Prima Additive business division of Prima Industrie, with the objectives of design, development, engineering, production, marketing, installation and technical assistance of mechanical, electrical, electronic, and optoelectronic machinery, equipment, systems and plants. It was born with the aim of attacking a rapidly expanding market, that of the AM of metal parts. The company has drawn up a very accurate development plan by first identifying the needs of industrial customers in various sectors such as aerospace, automotive, jewelry, oil&gas and medical, and subsequently the technical solutions capable of satisfying these needs. Today Prima Additive is a large company, owned by Prima Industrie S.p.A.

Machines

Prima Additive develops, manufactures, sells, and distributes industrial systems for metal AM applications. The Prima Additive product portfolio includes the two largest laser technologies on the market for metal 3D printing applications. Solutions PBF e DED (Figure 24). The company develops AM both through strategic partnerships and through innovative solutions.

Figure 16: Prima Additive product portfolio

Compatible materials

The powders that Prima Additive uses (Table 6) are tested extensively to provide a good understanding of the mechanical characteristics of the part.

Table 4: Materials used in Prima Additive Macchine

POWDER BED FUSION TECHNOLOGY	DIRECT ENERGY DEPOSITION TECHNOLOGY
STEEL ALLOY	
316L	316L
M300	M300
H13	H13
ALUMINUM ALLOY	
AlSi10Mg	AlSi10Mg
NICHEL ALLOY	
IN625	IN625
IN718	IN718
Hastelloy X	Hastelloy X
TITANIUM ALLOY	
Ti-6Al-4V	Ti-6Al-4V
Cr-Co ALLOY	
CoCr	N/A
COPPER ALLOY	
CuSn10	N/A
Cu	N/A

3.2 Print Green 150

The thesis topic is mainly focused on the development of new applications printed with Prima Additive machines, based on the PBF technology previously described; in particular, this work has involved the use of the Print Green 150, the small-size machine available in the Prima Additive portfolio.

Figure 25 shows the machine used to achieve the objectives proposed in this thesis work.

Figure 17: Prima Additive Print Green 150

An innovative open configuration powder bed additive system consisting of a cylindrical work area, a preheating system, real-time monitoring of process parameters and laser spots.

A compact AM machine for manufacturing small components.

Thanks to the possibility of customizing the process parameters, Print Sharp 150 is also the ideal solution for those looking for a machine on which to carry out research on new materials.

The Prima Additive PBF solution equipped with a green laser, functional for the processing of materials highly reflective, such as pure copper or precious metals: ideal for the electronics and Jewelry sectors.

This is because the wavelength of the green laser is presented as optimal for the fusion of these materials with quality and clearly superior repeatability compared to solutions equipped with infrared lasers.

Main Features

- ✓ Variable focus position of the laser beam according to need, to always have the parameters optimized according to the application.
- ✓ Double pre-heating system which allows to heat the surface of the powder bed both from above and from below.

- ✓ The high-speed coaxial pyrometer monitors the temperature in real time and cameras monitor the process and the powder bed.
- ✓ Open parameters, suitable for carrying out research and development on processes and materials.
- ✓ Easily adjustable filter unit thanks to the control installed on the interface.

3.3 System Setup

AM processes follow many of the same manufacturing steps observed in more “traditional” manufacturing processes, from design to manufacture to inspection. As an advanced manufacturing process, AM introduces new complexities to those same steps. AM-specific information is necessary to specify, verify, and archive parts that are manufactured using AM technologies. Key information associated with those steps includes relevant facility, operator, machine, process, material, and other information. As a digital manufacturing process, AM requires unique digital representations of the information associated with each of those steps and a means to manage these representations.

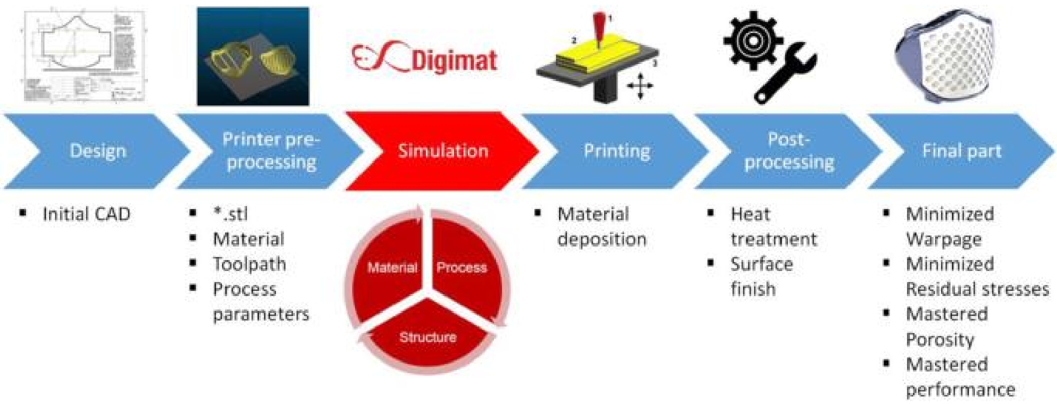

Figure 18: Illustrative additive manufacturing workflow

Figure 26 represents the workflow of a part fabricated using an AM process. The information requirements associated with individual steps in that process provide a reference as to which AM parts can be designed, procured, manufactured and inspected. Using a digital thread as a reference, the selection of information requirements for a specific scenario forms the basis upon which an AM data packet is formed. A data packet is an organization of selected information outlined in the digital thread.

3.3.1 Laser Setup

Closely derived from the Print Sharp 150, which uses a 200 W IR fiber laser, the Print Green 150 features a unique 200 W fiber laser working with a wavelength of 520 nm; contrary to a common infrared laser, characterized by a wavelength of 1063 nm, a green laser can melt highly reflective and low energy density materials, as materials such as copper and precious alloys have their peak in the absorption spectrum at is roughly in the range of 500-600 nm.

Why Green?

Improve the laser melting process of reflective materials:

- ✓ Identical **material properties** to bulk material
- ✓ Higher **Efficiency, lower energy consumption** and higher **Productivity** (for high reflective materials)
- ✓ Higher **Density** values
- ✓ Better **Roughness** values
- ✓ Enable **new Applications**: copper alloys increase copper mechanical strength, combining highly conductive material properties with the needs to support structural strength, for example in large combustion components for **Aerospace**, or inductors for **Oil & Gas** or **Electronic Components. Gold for jewelry.**

3.3.2 Powder Deposition System

With a circular platform of 150 mm in diameter, heat able up to 200 °C, and a maximum building height of 160 mm, this machine is perfect to produce small parts with high surface quality and high relative density, making it feasible especially for automotive, aerospace and jewelry industries. Figure 27 show the PG150 powder deposition system.

Figure 19: Powder Deposition System

Main Features:

- **Green fiber laser**, fiber 200 W Green, 532nm wavelength, QCW, Single Mode, gaussian beam, whit a spot size of about 35 µm
- Laser focus diameter, 35 - 100 µm (adjustable focus position).
- **Pre-heating** from the top through incoherent light system and from the bottom of the powder bed up to 250 °C to allow better casting performance.
- An **optical system** with beam expander, to change the spot size of the beam laser as needed.
- **Automatic adjustment** via software of the laser beam focus position on the platform, to obtain an optimal result depending on of the application.
- **High speed** coaxial pyrometer for bed temperature control.
- **2 cameras** for process monitoring, one visible and one infrared.

- ➢ **Open Process parameters** and suitable online setting.

Best for copper ang gold applications.

3.4 Process parameters

The process parameters that most influence the final product deriving from AM production technology are detailed below. It is necessary to make an initial subdivision between the factors that affect the final product: those that intrinsically depend on the material used, factors that therefore cannot be modified during construction, and those that depend on the production process (Tab. 7).

Table 5: Breakdown of process parameters

Unalterable parameters	Process parameters
Thermal conductivity	Laser power
Specific weight	Point size
Fusion point	Scan speed
	Distance between tracks
	Scan strategy
	Supports
	Preheating

In powder bed processes, the process parameters can be divided into three categories:

- Parameters relating to the use of the laser (power and spot size).
- Scan parameters (speed, distance between tracks and scan strategy).
- Parameters related to the physics of the process (type and number of supports, orientation, atmosphere, preheating).

3.4.1 Laser parameters

Laser power (P)

Power is the first energy parameter that strongly influences the final density of the component. Usually, the power range used in PBF processes is 200 – 1000 W. To set the correct power value it is first necessary to know the scanning speed. Power indicates the amount of energy transferred per second, so speed directly affects the time spent in the same area. All other parameters being equal, as the power increases, the density of the material increases. On the other hand, the density decreases slightly if balling phenomena occur or if the flow velocity in the pool is too high, which favors gas trapping. In general, powers that are too low does not allow for correct penetration of heat and therefore cause failure to re-melt the previous layers, with consequent lower adhesion between the layers. Furthermore, the maximum temperatures reached are lower and with them the viscosity of the liquid metal also decreases. The viscous molten metal has poor wettability and is unable to penetrate the voids but tends to form metal agglomerates surrounded by areas of non-fusion.

Spot size

The laser is idealized as a perfect circle that engraves the powder bed causing localized melting. This circle has a radius; therefore, an area is affected by the amount of powder heated by the beam. The larger the radius, the greater the amount of powder affected. With the same quantity of powder used, different results can be obtained in the final product, by varying the dimensions of the incident laser spot. Even the powder is not uniformly distributed within this spot area, as you move away from the center, the energy decreases. To know the real dimensions of the involved area it is necessary to make a characterization of the laser propagation. This type of analysis is performed with individual parameters depending on the type of laser used, therefore it is the responsibility of the printer manufacturer to provide this information.

3.4.2 Scan parameters

Scan speed (v)

Scan speed is the speed at which the laser beam moves and is measured in millimeters per second. The scanning speed has an opposite effect compared to the power, in fact, an increase in it increases the presence of consolidation defects. The interaction time between the laser beam and the surface decreases and therefore the temperatures involved, and the depth of the melt pool decreases. Therefore, the lower this speed is, the longer the laser remains in the same point, and this involves too much energy which will evaporate the powder causing porosity. For these reasons, the scanning speed value must be chosen very carefully, bearing in mind that it could vary according to the applied power and the printed material, assuming values from 300 to 2500 mm/s.

Distance between tracks (t)

To melt the powder, the laser beam moves along the desired area making straight lines. The distance between two adjacent traces is called the trace distance. This distance is measured in millimeters and can assume values between 0.05 and 0.25 mm.

When the laser beam hits the powder bed, a specific area absorbs energy and the material melts. This area can be idealized by a circle, the surface of which depends on the diameter of the beam.

The trace distance refers to the distance between the centers of adjacent traces. As with layer thickness, the higher the tracing distance, the higher the progress of the process and therefore the higher the productivity. If the tracks are too far apart, the powder between them will not be fully merged. Also, since the laser melts circular areas, the outer areas usually have lower energy than the center; this means that these areas are not completely melted, which is why the traces must be closer to each other. The effect of the distance on the final density finds an asymptotic trend and the influence becomes negligible for almost all materials with an overlap of 50 %, or less in the case of a penetration high enough to guarantee the re-melting of several layers.

Layer thickness (h)

AM technologies produce 3D parts by adding 2D slices layer by layer, therefore, at some points in the process, the distance between each layer must be set.

This distance is called layer thickness and has values between 0.02 and 0.1 mm. The higher this value is, the faster the production process will be since, for the same height, fewer layers will be required. To compare production processes, reference is made to a factor that shows the volume of material produced per hour, normally expressed in cm^3/h. This factor is calculated with the product of the layer thickness, the distance between the traces and the scanning speed.

$$B = h \times t \times v \tag{7}$$

As can be seen, the degree of construction B (Equation 7), is directly proportional to the thickness of the layer. When setting the process parameters, it must be considered that an increase in layer thickness means an increase in productivity, but it cannot be increased indefinitely, as other problems linked to the properties of the final component can be encountered.

Scan strategy

In the PBF process, the scanning strategy will have a major impact on the forming quality and dimensional accuracy of metal parts. Common scanning strategies include unidirectional scanning, zigzag scanning, spiral scanning, and island scanning, as shown in the Figure 28.

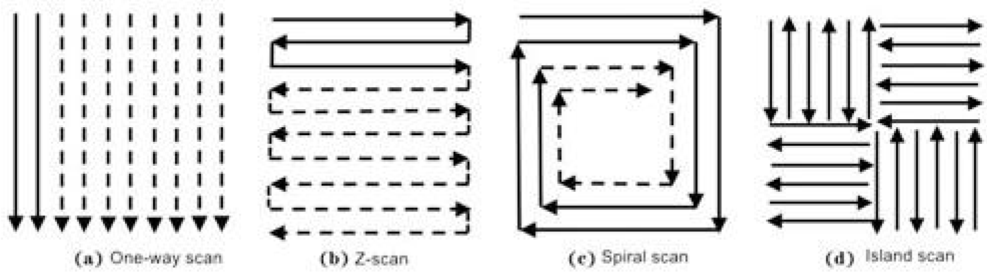

Figure 20: Scan Strategy [h]

Unidirectional scanning and Z scanning are relatively simple traditional scanning strategies. The heat transfer in the helical scanning process is more uniform than that of unidirectional and Z-shaped scanning, so the generated temperature gradient is smaller, the temperature field is more uniform, and the residual stress and strain of the final parts are also minors. Island scan strategy refers to a strategy that divides the area to be scanned into multiple small square areas, and then scans these islands according to a preset scanning sequence. The island scanning strategy makes the heat distribution in the machining process more uniform and reduces the heat concentration; and the adjacent islands of the upper and lower layers have mutually perpendicular scan directions, which reduces the anisotropy between different deposition layers and the entire metal parts. Helps reduce warping of additively manufactured components. Studies have shown that scanning at a certain angle (usually 67° or 90°) between layers can also reduce anisotropy between deposited layers, improve interlayer adhesion, and reduce delamination and warping.

3.4.3 Parameters related to the physics of the process

Supports

The choice of supports is a very important parameter because it must guarantee that the component remains anchored to the building platform during the process. Without the supports it would be impossible to detach the component from the plate, this operation would require that the component should be designed with the allowance along the entire support area. The supports, therefore, must have a sufficient height to separate the piece from the base and to provide for a simple and non-destructive detachment for the surfaces of the component itself.

The usefulness of the supports, however, is not limited to that of interposing between the piece and the base, but it is necessary to consider the reasons that sometimes prevent their correct anchoring: the formation of residual tensions and deformations. The choice of supports must take this aspect into account and favor correct heat dissipation. In particular, the areas at greatest risk of deformation are the cantilevered ones because the thermal conduction towards the central volume of the component is limited and the powder has a coefficient of thermal conduction, compared to the corresponding solid material, two orders of magnitude lower (Rombouts, 2005). For this reason, the protruding material volumes are subject to strong overheating and lead to the formation of residual stresses. The presence of supports for these areas allows for heat dissipation, but not only that: the underlying dust, in addition to not being a good thermal conductor, is not even sufficient to support the solid component.

Some scientists (Chivel, 2011) have carried out an experimental campaign to determine the temperatures involved and the problems related to the undercut or protrusion of some areas of the components. The authors have come to affirm that the instability between the molten material of the undercut area and the underlying powder is linked to the Rayleigh-Taylor phenomena whereby the denser upper material tends to descend and mix with the less dense one. For all the reasons described above, the geometries and dimensions that today it is possible to use to support the PBF manufactured components (Figure 29), also relying on those already foreseen in the process management software, are numerous.

Figure 21: Supports [i]

Preheating

According to (Bey Vranken, 2012; Brunkner, 2007; Luke, 2014; Michael F. Zaeh, 2010), it is confirmed that the preheating of the powder by heating the base plate reduces the residual stress.

The several studies mentioned above found that in the laser AM process, the substrate distortion along the deposition direction (Z direction) is much greater than the other two directions (X and Y directions), and the substrate deformation caused by machining laser is permanent and cannot be heat treated.

Preheating the substrate can reduce the temperature gradient and cooling rate during the forming process, thereby reducing the residual stress and strain of the formed part. Furthermore, it was found that the degree of buckling deformation of the cantilever beam decreases with increasing substrate preheating temperature; and the use of substrate preheating can effectively reduce the residual stress, and the residual stress increases with the preheating temperature in a certain temperature range. If the height is reduced, the deformation of the formed part is also reduced.

At present, substrate preheating has become an effective method to reduce residual stress and deformation of the formed part, and in situ annealing of the layer deposited during the forming process provides a new way to control and solve stress problems residual and deformation.

3.5 Scanning Electron Microscope (SEM)

The microstructure analysis of the samples made is performed using the scanning electron microscope (SEM) thanks to which it is possible to evaluate the morphology of various types of samples.

3.5.1 Operating principle of the Scanning Electron Microscope (SEM)

The scanning electron microscope is a device which, exploiting the interaction of electrons with matter, can acquire the image of the surface of a sample by enlarging it up to millions of times.

The architecture of the instrument (Figure 30) foresees the presence of two essential parts:

- A cylindrical block containing various elements such as a tungsten filament, coil systems and condenser lenses.
- A base on which the sample holder is placed in which the specimen is present as well as a series of sensors able to detect the electrons that are deflected according to different modalities.

The instrument is equipped with a processing unit that allows the assignment of the information necessary for the execution of the test and the movements along the surface of the sample. It is equipped with a CRT (cathode ray tube) monitor on which the image scanned by the instrument is displayed in real time.

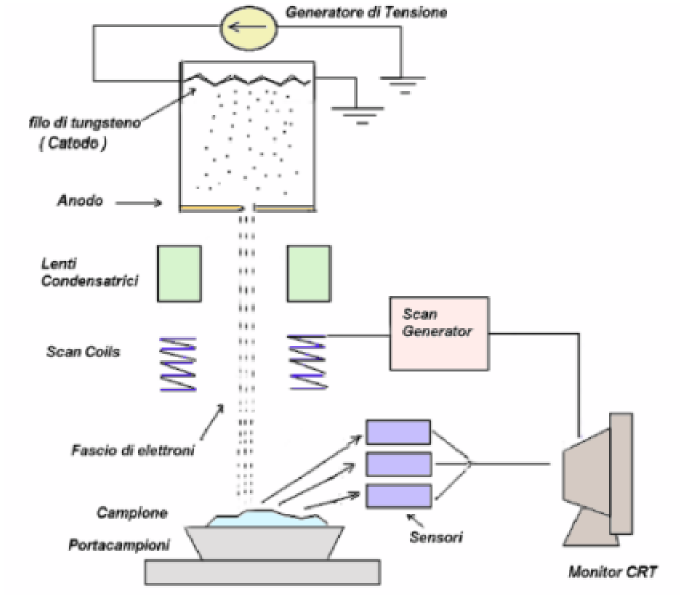

Figure 22: Schematic of a scanning electron microscope SEM

The SEM operating principle is characterized by multiple stages.

Inside the cylindrical block there is a tungsten filament which, when heated, is able to emit a beam of electrons; it is suitably accelerated as a result of a potential difference applied to the ends of the filament, which acts as a cathode, directing the electrons towards a perforated plate, which acts as an anode.

It is evident that it is possible to adjust the emission speed of the electrons by varying the applied voltage (its value can oscillate between 1KeV and 50KeV). The electron beam, before reaching the sample, is previously "focused" through a system of condensing lenses and directed by the effect of the magnetic fields present inside coils (scan coils) crossed by currents fed by a generator (scan generator).

The electron beam reaches the surface of the sample where interaction phenomena occur between electrons and matter and the emissions are detected by appropriate sensors, which transfer the signals, duly converted, to a CRT monitor. The detected image is made up of many bright "spots" whose intensity is linked to the intensity of the emissions; in particular, the presence of lighter areas is due to emissions relating to elements with a higher atomic number and therefore capable of emitting more electrons, while the darker areas refer to emissions relating to elements with a lower atomic number. A fundamental parameter in the evaluation of a SEM micrograph is the enlargement defined as the scale ratio between the dimension of the scanned surface element b and the dimension L of the corresponding segment displayed on the monitor. It is evident that, as the magnification increases, and therefore as the section b of the specimen along which the scan takes place decreases, the interactions between the electron beam and the sample increase, since the electrons interact on increasingly smaller portions of the surface, which entails an increasing difficulty in focusing the image.

Chapter 4

HYPOTHESIS AND RESEARCH OBJECTIVES

4.1 Research Novelty

What has been said so far is a still unexplored field, especially as regards the use of a green laser source in the AM process instead of a common infrared laser source. One of the first steps to be able to effectively evaluate the quality of the printing process using precious alloys is to start from a knowledge base both from literature and from experience with materials of similar chemical composition, if possible.

The challenge

Using infrared laser to print copper and gold, which are highly reflective materials, shows several limitations such as:

- Low absorption.
- Unstable process.
- Low efficiency and performance.

Indeed, as seen previously, pure copper and gold have a higher absorbance when the wavelength is in the spectrum is shorter (green or blue).

4.2 Research Aim and Objectives

The main objectives of this thesis are two:

Goal 1:

Industrial use case: ***Printing a Copper component of the Combustion Chamber of satellite launcher.***

Sector: *Space*

Details: *Confidential case study developed with industrial partner*

Goal 2:

Industrial use case:

2a. Copper & Gold printing for jewelry components.

2b. Gold wire welding.

Sector: *Jewelry*

Details: *Confidential case study developed with industrial partner*

With the aim therefore of wanting to apply an approach as homogeneous as possible for the development of a new methodology for printing precious metals. At the same time, however, there is the need to want to reduce the consumption of material used for the tests, in fact these are very expensive materials. For this reason, indeed, it was decided to use, for the second case study (Jewelry), as a starting point the knowledge acquired with copper printing observed for the first case study (space).

4.3 Research Methodology

The research methodology employed for qualifying materials for PBF process, processing and analysis which are explained in detail below:

4.3.1 Material Selection and Characterization

The preliminary process of studying new process parameters was also supported by two important multinational companies. The first is the leader for the space sector to produce satellite launchers. The powder used for this case study is pure copper. The second company is one of the biggest companies in jewelry sector for the production and sale of artefacts in precious materials, obviously including gold and silver, and which supplied the raw material necessary for their business. In particular, the powder used is obtained from red gold, i.e., a gold alloy which, having a fair amount of copper inside, responds in theory to green laser fusion in a similar way to pure copper already used for other applications industrial. Furthermore, for this second case study, welding tests of gold wires on gold plates with a blue laser were also performed.

Table 8 shows the chemical composition of red gold used in this study.

Table 6: Chemical composition of red gold

Element	Percentage
Au	75%
Ag	2.5%
Cu	21.7%
Zn	0.8%

The gold particles have a diameter of about 12÷25 µm, the gold powder was found to be mostly spherical in shape with smaller satellite particles agglomerated to the larger particles.

The development activity was therefore carried out starting from a feasibility case study related to the printability of red gold, then the assessment of the most suitable process parameters. Consequently, the optimization of process parameters was carried out in order to perform some tests on pure copper; an important part of this work has been the implementation of some previously shown concepts, to get as close as possible to the needs of the goldsmith and space sector.

4.3.2 Processing

Following the definition of the build layout, the CAM software generated a file in a format suitable for applying a specific set of process parameters; since the entire process is based on the selective fusion of layers of powder, the software in question proceeded to create slices of the component, each with a thickness corresponding to the thickness of the layer of powder spread by the recoater. For each layer, the number of parameters that can be used is high, which is why the most important parameters that have been entered are shown below, and which decisively influence the relative density of the material and the quality of the entire process.

Furthermore, the parameters associated with the environment variables of the process chamber are of fundamental importance for the purposes of printing the detail; specifically, for example, the inert gas used was argon as, unlike nitrogen, it does not react with gold and copper at both low and high temperatures, avoiding any possible risk associated with exothermic and therefore potentially explosive reactions.

The AM process is much more complex, and it can be broken down into different main steps:

Step 1: Using CAD Software to Design a Model

Step 2: Pre-Processing

Pre-processing covers a range of steps that must be completed between design and manufacturing. It covers two primary activities:

1) Preparing Files for 3D printing

Once a 3D design has been tested and signed off, it is ready to be prepared for printing. To do this, a hurdle must be overcome: interoperability. Interoperability is the ability of different computer systems to exchange and make use of information. In the AM process, the problem is simple - manufacturing machines like 3D printers dont 'understand' CAD files well enough to enable the manufacturing process.

To overcome this, a file must be converted into a set of instructions that can be understood by AM hardware. These instructions are created using 'slicer' software such as Spatial's CGM Polyhedra which converts the 3D design into 2D layers or slices which can then be used to calculate the tool path or G-Code needed to manufacture the object.

2) Simulation modeling

Simulation modeling is used to digitally test 3D designs before they are manufactured. These tests are used to determine the real-world structural integrity of an object - i.e., whether it is likely to fail, how it might fail, and what forces it can withstand without failing. The simulation allows to simulate the structure, process, and materials of the component to be printed.

Common simulation modeling techniques include Computational Fluid Dynamics (CFD), Finite Element Analysis (FEA), and Non-Linear Stress Analysis.

Step 3: Printing

- A layer of material, typically 0.1mm thick, is spread across the build platform.
- A laser fuses the first layer or cross section of the model.
- A new layer of powder is spread over the previous layer using a roller or a recorterblade.

- Additional layers or cross sections are merged and added.
- The process repeats until the entire model is created. Loose, unfused powder stays in place but is removed during post-processing.

Step 4: Post-processing

The post-processing step generally involves heat treatment and surface finishing (reduction of roughness by sandblasting and/or polishing).

The metal parts made using PBF technologies have levels of finish and tolerances (geometric and dimensional) comparable to those obtainable using traditional foundry techniques. This requires reworking of the machine tools which must be carried out considering on the one hand the characteristics of the processed materials (often difficult to chip), on the other the unconventional geometries allowed by additive technologies. Furthermore, in some applications, it is necessary to carry out post-treatments to improve the metallographic and mechanical characteristics of the product.

Step 5: Final part

Minimize deformations and residual stress, control porosity and performance.

4.3.2.1. Experimental setup

The experimental setup consisted of setting-up of the equipment: Prima Additive PBF system. This section explains the laser specifications and powder deposition mechanism for the Print Green 150 machine.

Machine features:

- Layer thickness 0.02 mm - 0.12 mm
- Laser focus diameter 35 - 100 μm (position adjustable)
- Pre-heated plate up to 200 °C (300 °C optional)
- Technical gases Nitrogen, Argon
- Total dimensions of the system 1760 x 1120 x 2200 mm
- Machine weight 1800 kg
- Power supply 380V/50Hz /6kW/32A

4.3.2.2. Identifying suitable processing parameters

To find suitable process parameters for melting red gold with the green laser, some reference values used to produce pure copper components have been chosen, and with which it has been possible to obtain consistent results in terms of both relative density of the material and surface roughness (Figure 31).

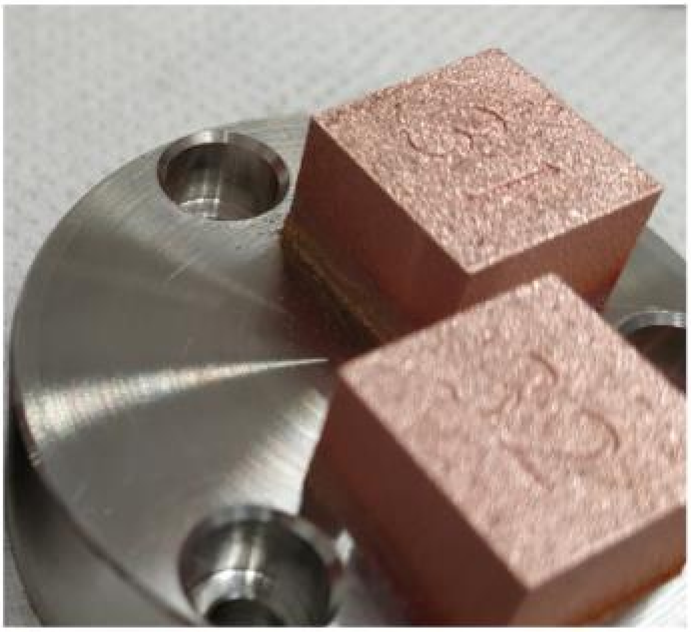

Figure 31: Copper Design of Experiment for density

Having identified the best laser power and speed values, which most influence the progress of the printing process, these were used to verify the printability of the red gold, whose Design of Experiment only concerned the creation of a few cubes for measuring density by metallographic analysis.

Using a modified version of the build platform, a smaller version to limit as much as possible the amount of precious powder to be used, the recoater, also smaller, and a removable compartment to remove excess powder at the end of the process, a small batch of specimens was produced, also using environmental parameters equal to those used with copper.

The machine parameters used to print the red gold cubes shown in Figure 32 are shown in table 9.

Table 7: Machine parameters for red gold

Platform Temperature	80 °C
Oxygen concentration	0,05%
Layer thickness	30 µm
Hatch DIstance	0,12 mm
Laser Power	180 W
Scanning Speed	750 mm/sec

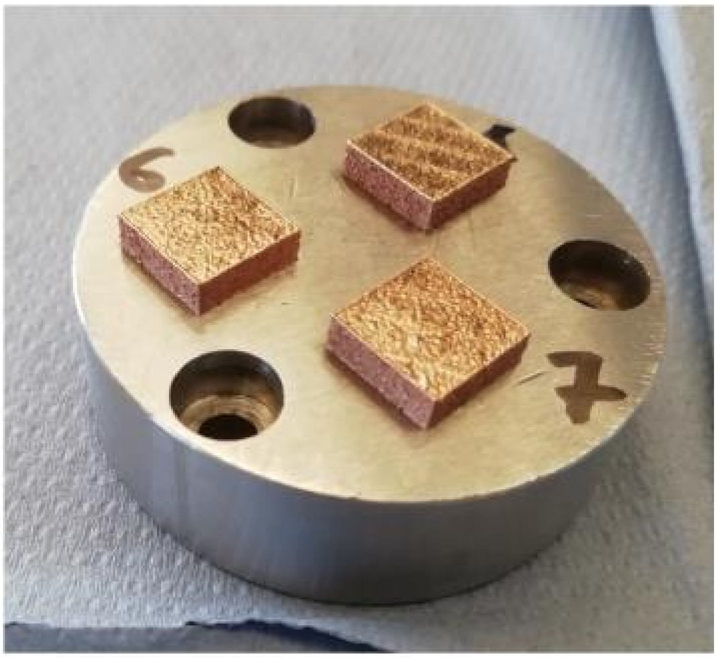

Figure 32: Red gold samples

Once the processability of the gold by means of a green laser had been verified, the first process parameters obtained, although not optimized, were in any case used for the printing of a particular product by means of investment casting by the multinational partner of the research.

In particular, the component referred to is a ring which (Figure 33), for reasons related to the preservation of intellectual property, is shown in this work in a simplified form, and therefore not fully explanatory of the results obtained relating to the original component.

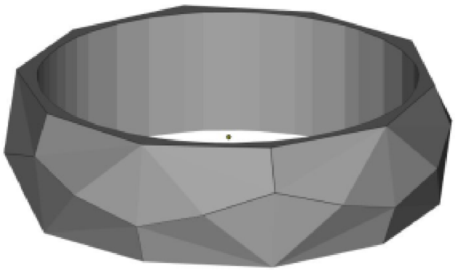

Figure 23: Simplified model of a gold printed ring

4.4 Gold Laser Blue Welding

Goal 2b concerns Wire Deposition of gold by multimode blue laser, to test the solderability of gold using a short wavelength laser, in the blue region.

The reason why a blue laser is used with a material such as gold is that compared to an IR laser it is 55 times more efficient.

The tests were conducted using gold wires with a diameter of 1 mm to be welded on plates of the same material with a thickness of 0.5 mm and a width of 40x40 mm.

8 gold wires were placed on the gold plate and fixed on the moving platform in z of the laser system. The process and handling parameters have been set on the Zaber software. In particular, the parameters of speed, voltage, current position, emission start position, emission end position, start position, end position have been entered, which are the initial and final positions of the laser stroke (Figure 34). The welding process took place in a controlled atmosphere with argon. The laser spot was varied between 150 ÷ 200 µm by moving the support platform along the z axis.

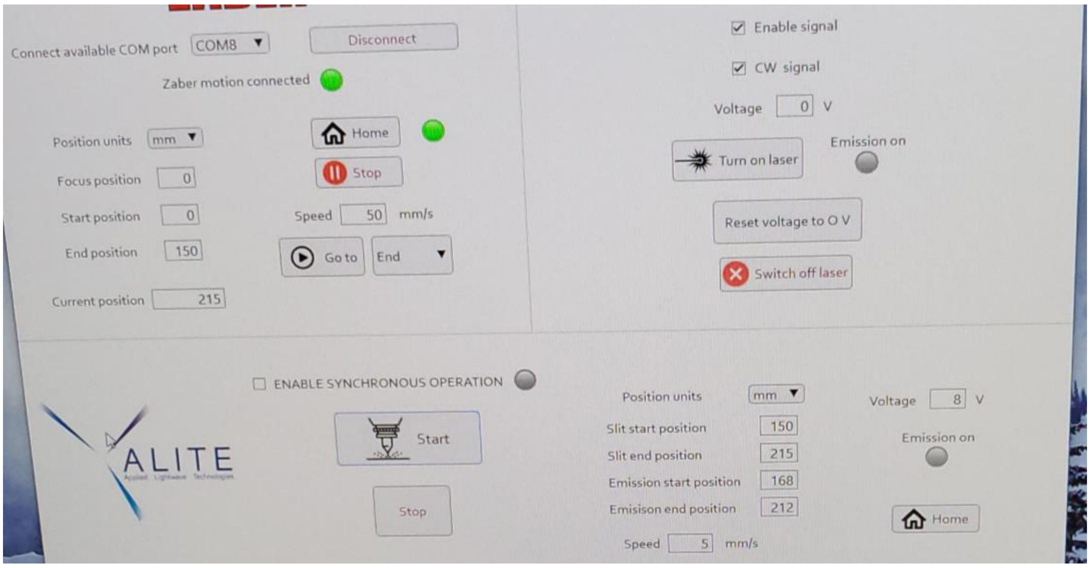

Figure 24: Gold Welding Parameters

Table 10 shows an example of parameters chosen for one of the tests performed.

Table 8: Example of process parameters for test 5

Parameters	Set Value
Power	140 W
Speed	5 mm/sec
Voltage	8 V
Spot	175 µm
Emission Start Position	168 mm
Emission End Position	212 mm

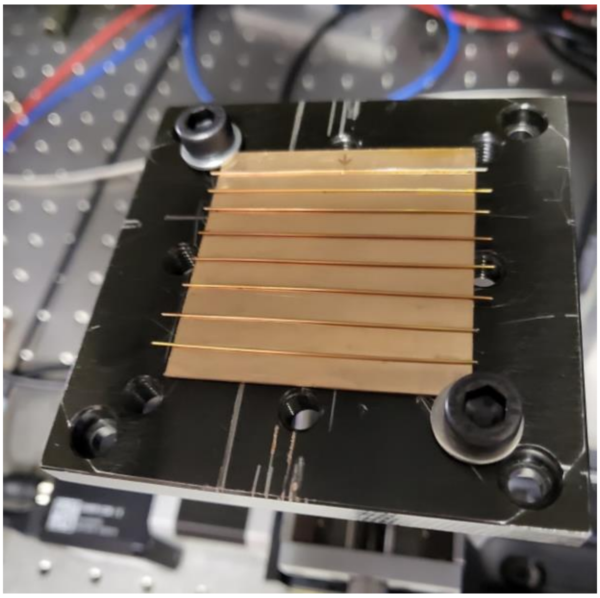

Figure 25: Welding System

About 24 welding tests of gold wires on gold plates were carried out (Figure 35). The various tests were carried out by varying the speed, the power of the laser and the distance of the focus, all in an inert atmosphere using argon. The plate was previously heated to a temperature between 80 and 90 °C to facilitate welding process. The laser used has a power of about 200 W, the other characteristics of the laser are shown in Table 11.

Table 9: Features of the blue laser

Optical Parameters	Units	AO-150 Typical
Wavelength	nm	~450
Bandwidth	nm	~10
Output Power	W	180
Power Adjustment	%	0 - 100
Power Stability (8 hours)	%	<3% at full power
Fiber Diameter (Core)	µm	200
Fiber Numerical Aperture	NA	0.22
Beam Product Parameter	mm-mrad	<15
Standard Fiber Length - Connector Type	m	5 - QBH

Chapter 5

ANALYSIS AND RESULTS

5.1 Analysis

Density analysis (SEM - Scanning Electron Microscope)

About 24 specimens with different parameters were printed to identify more and better parameters to print the copper (Size of the cubes is 15*15*15mm).

The data obtained have repeatability equal to 2 (two tests for each print in which we found the same values). In Table 11 the density data relating to the specimens with the best parameters are reported. Excellent density can be observed for all samples.

Due to a considerable number of sets of different process parameters, for copper the 4 sets that returned the best results in terms of density following the laboratory analyzes were initially identified, which are shown in Table 12.

Table 10: Check on density for pure copper

Specimen number	Medium porosity [%]	Standard deviation σ	Max Density [%]	Min Density [%]	Medium Density [%]
#1	1.51	0.87	99.57	95	98.48
#2	1.33	0.62	99.44	96.18	98.66
#3	2.46	1.59	99.51	91.08	97.53
#4	1.3	0.6	99.6	96.3	98.72

Copper roughness results (Roughness Tester)

The best set of process parameters was then further tested to produce inclined specimens, to evaluate the effect of the undercut on the surface roughness.

The roughness was calculated in the down skin part of the sample. Also, in this case the repeatability is equal to 2.

The samples with different inclination angles were printed and analyzed. In the Table 13 it can see that the maximum roughness decreases for larger angles.

Table 11: Check on roughness results for pure copper

Specimen number	Medium roughness [Ra]	Max roughness [Ra]	Min Roughness [Ra]	[Rz]
#1 (vertical)	4.7	7	2.4	36
#2 (45°)	6.97	7.3	6.3	40
#3 (48°)	6.73	7.1	6.2	41.5
#4 (51°)	6.57	6.8	6.3	34.5

Metallographic Analysis

Once the printing process, which lasted about 3 hours, was completed, the specimens were extracted from the process chamber, to then be subsequently removed from the building platform by wire cutting and subjected to metallography.

In particular, the metallographic analysis showed that, despite the first attempt to work red gold with a green laser source, the material had a behavior very similar to that of copper; however, the heavy presence of gold within the alloy inevitably created zones of uneven melting, which can be mitigated by further optimize the process parameters, to do this it will be necessary to conduct further experiments, varying the parameters and searching for those that best meet our needs.

The results obtained are shown below (Figure 36 and 37):

- Relative density equal to 98,93 %.
- Localized porosity along the stripe.
- Maximum porosity equal to 160 μm.

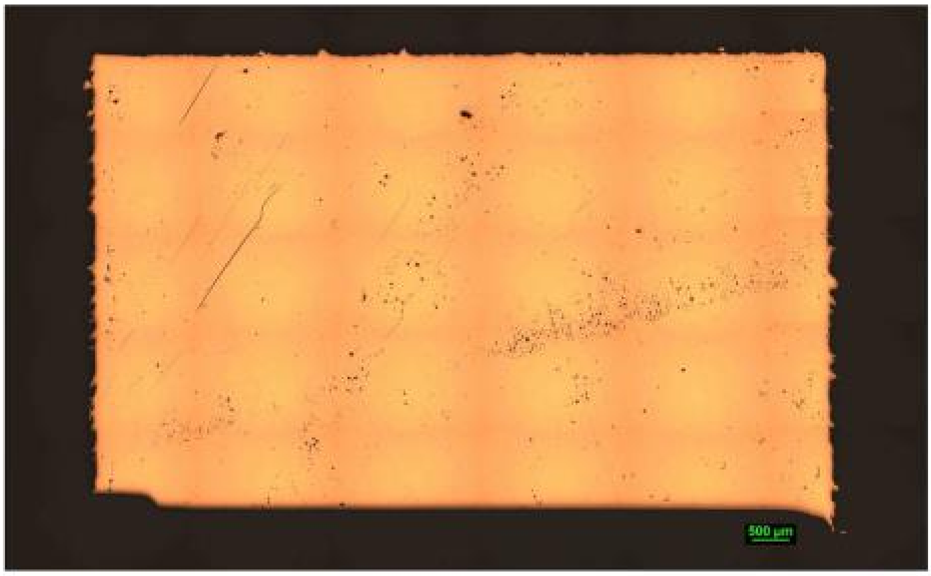

Figure 26: Top view of metallographic analysis

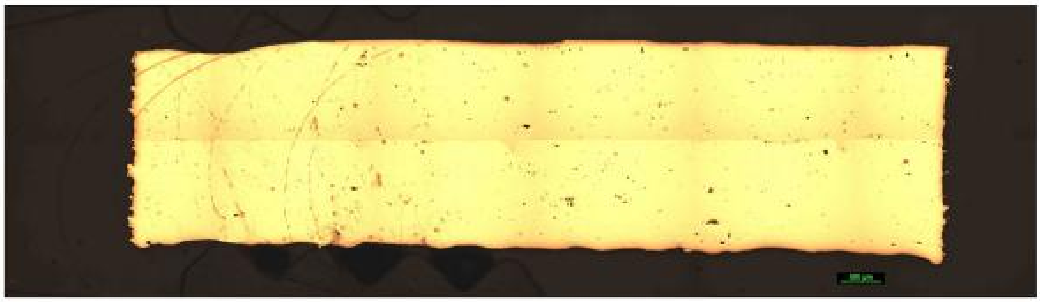

Figure 27: Side view of metallographic analysis

Gold roughness results

The ring printed, was analyzed above all under the aspect of surface roughness (Figure 38), a critical aspect which characterizes every goldsmith's production.

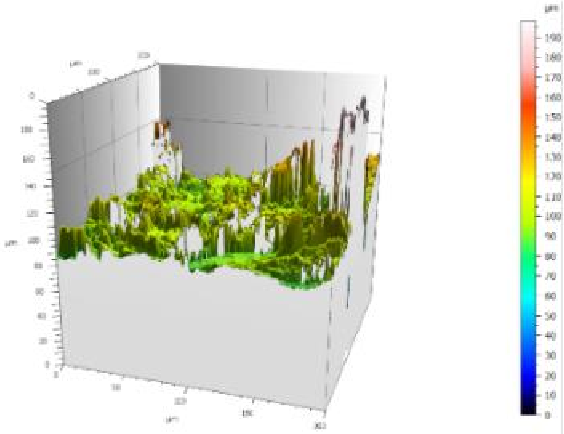

Figure 28: Surface roughness analysis of a 3D printed gold ring

The analysis, which is influenced by high waviness and point asperities given by sintered powder particles, gives back values that go from 12 to 23 µm, too high for the constraints of this type of applications.

Parameters optimization

Having obtained all the necessary information, therefore, the optimization of different aspects of the component printing process was evaluated as a next step by using copper powder; indeed, considering the very high cost of the raw material and the logistical difficulties relating to having to conduct research of this type within industrial contexts and not in locations specifically equipped for the handling of precious metal powder, the similarity between red gold and pure copper, seen during the printing of the samples in the previous paragraph, has allowed to continue the activity with a fair degree of repeatability of the process and transfer of parameters.

The aspects that have been most taken into consideration in this optimization phase are therefore listed below (table 14):

Table 12: Parameters optimization definition

Orientation	Support Surface	Roughness
Horizontal	Type	Border
Vertical	Process parameters	Downskin
Inclined		Layer thickness

Starting from the orientation, a fundamental criterion for the correct creation of surfaces with a high surface finish, the horizontal one was considered the best solution; considering that, unlike the simplified model previously shown, the original model has cantilevered structures on the entire side wall, the horizontal orientation allows not only to obtain reduced printing times and minimum material consumption, but above all to work with very thin walls, not very deformable due to the reduced height, and easily removable. The next step concerned the choice of supports, whose process parameters were kept the same as those of the part, and whose typology was chosen as a point solution, characterized by alternating thin walls whose intersection with the surface to be supported is just a point, with the aim of making the removal of the ring from the plate very simple by only detaching it from the supports with the minimum amount of residual stock. In this phase, the addition of the downskin parameters was also considered, i.e. specific laser powers and speeds for more inclined surfaces; the parameters were instead kept fixed with the reference values obtained with the copper already presented. By then fixing the geometry of the supports, and varying the process parameters relating to the downskin Figure 39, a DOE was created with various rings, analyzed using an optical microscope at the end of the print.

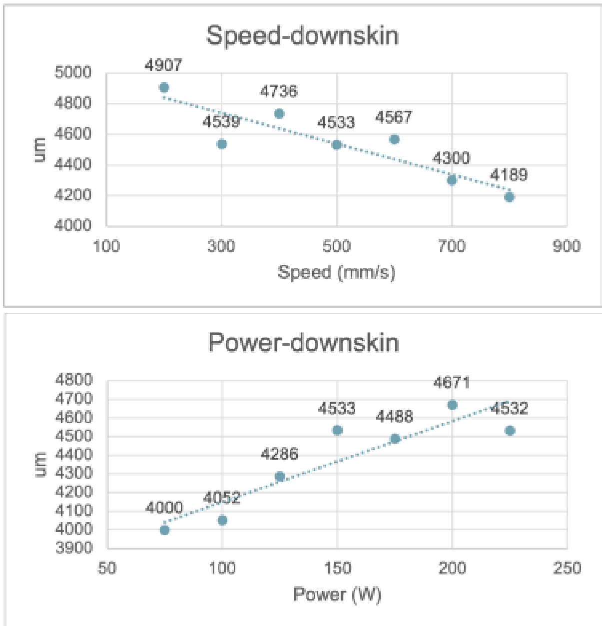

Figure 29: Influence of downskin process parameters on overhanging surfaces-Test 1

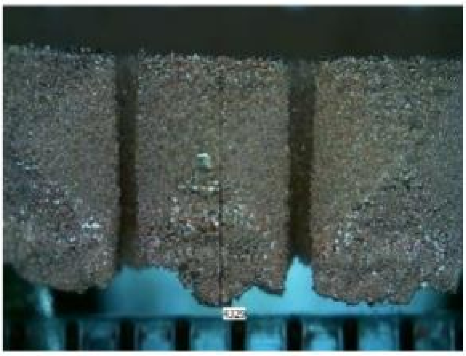

Figure 30: Surface dimensions deviation due to overhang

As a first measurement of the validity of the various process parameters relating to the downskin, the surface dimension deviation (Figure 40) between the nominal dimension of the overhanging features and the real one was measured for each ring; the result was that, for higher speeds and lower power, once all the other edge and inskin parameters were fixed, this deviation is reduced, thus keeping the desired geometry fairly unchanged.

The activity was then finished with a second print, in which the logic with which the support generation software selected the areas to be supported was modified; in previous prints, in fact, the supports were applied only to surfaces parallel to the horizontal plane, with the aim of limiting the number as much as possible. By changing the overhang angle relating to the generation of supports, now passing 45°C, a greater area is covered by support structures, and consequently is less subject to deformations deriving from the casting process. As can be seen in Figure 41 the deviation from the nominal dimensions, however present, has been further reduced, thus providing valuable information on how much the right compromise between the supported surface and the process parameters can lead to an overall improvement in the surface finish. The roughness obtained on the walls in contact with the supports, once measured, was also considered a good starting point for subsequent optimisations.

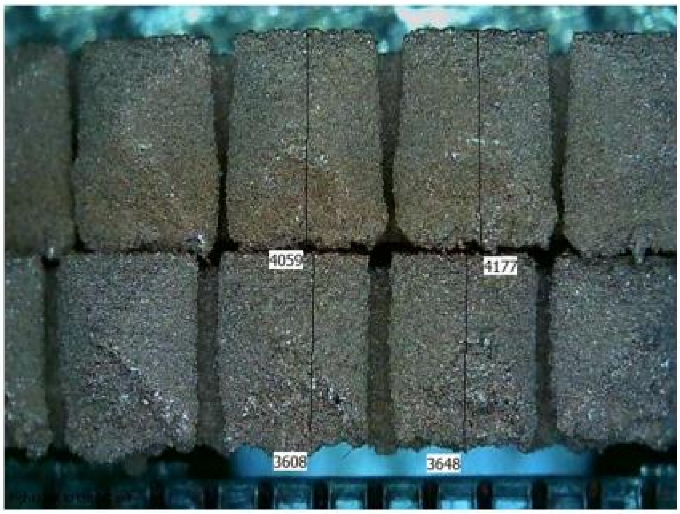

Figure 31: Surface dimensions deviation due to overhang-Test 2

5.2 Results AM Process

By comparing the results obtained with an IR laser and the first results obtained with the green laser, it is possible to highlight how this last type of laser source can bring great benefits in terms of quality of the components produced, such as relative density and surface quality, which are already superior those obtained with the IR laser, combined with an extreme increase in productivity.

In the figures below the density results found in the State of the art (SoA) (Lykov, 2020; IMAI, 2020; KHAN, 2010) using an IR source and the data found in this study using a green source, both for copper and for gold, have been compared.

The graph shown in Figure 42 shows the relative density obtained for copper, as the scanning speed and the power used vary. The best results are obtained using the green source, in fact a density of 99 % is reached, using the same speeds and less power.

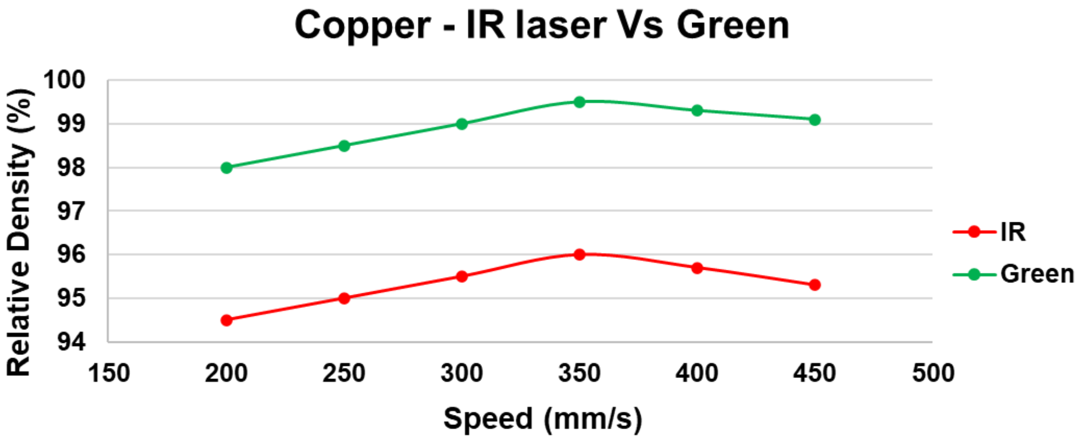

Figure 32: Comparison between IR and green laser source for copper production

The following Figure 43 shows the relative density obtained for gold, using an IR source. As you can see the densities are very low, the maximum is 85.5 %. The processing speeds of this material are also extremely low, which means very long times to produce a piece.

Conversely, Figure 44 shows how the relative density of gold increases, using a green laser. Furthermore, the processing speeds are much higher than in the first case, thus reducing production times and therefore increasing the productivity of the components.

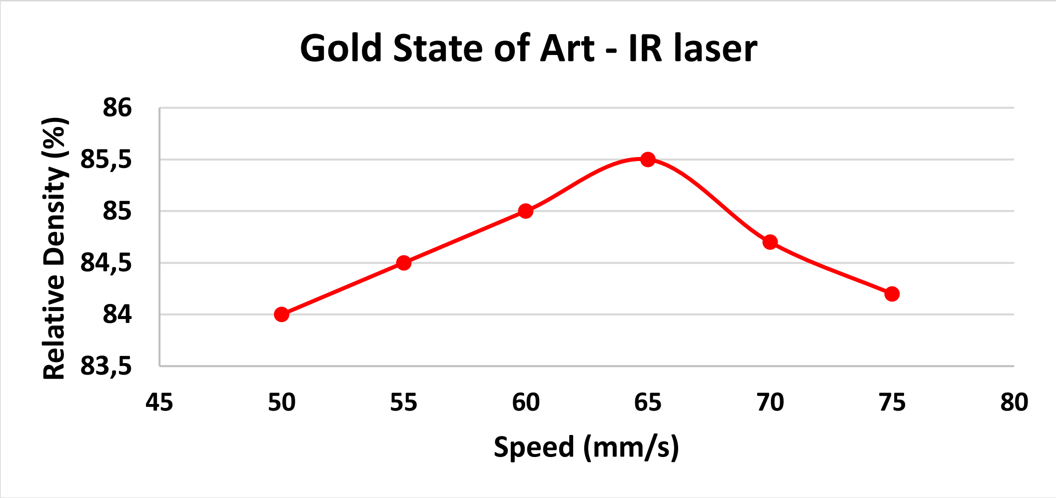

Figure 33: Gold SoA, (*KHAN, 2010)* – IR Laser

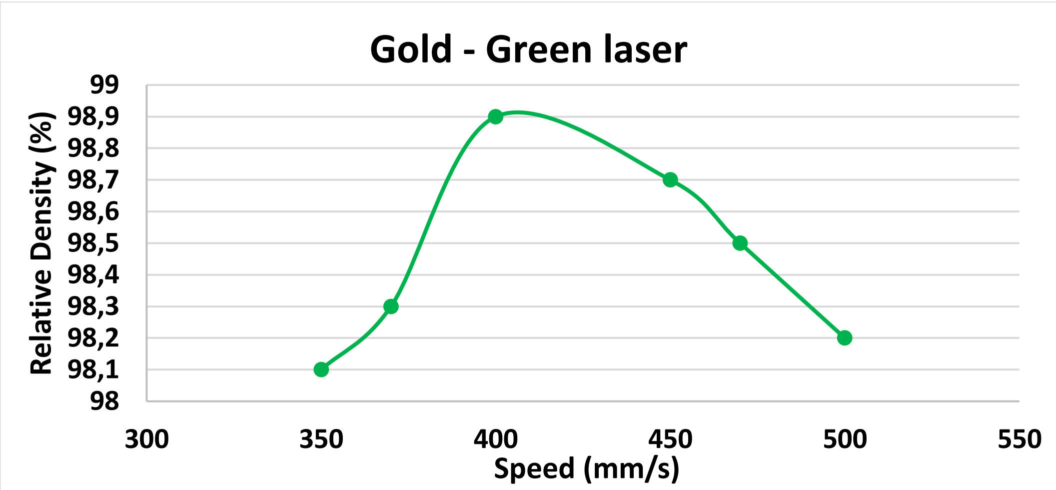

Figure 34: Gold – Green Laser

5.3 Results Welding Process

From the various welding tests of the gold wires on the gold plates, as the welding speed varies, it was visually found that the optimal condition is to use a speed of 3mm/sec (wire marked by the red rectangle in the Figure 45 below) at an intermediate power.

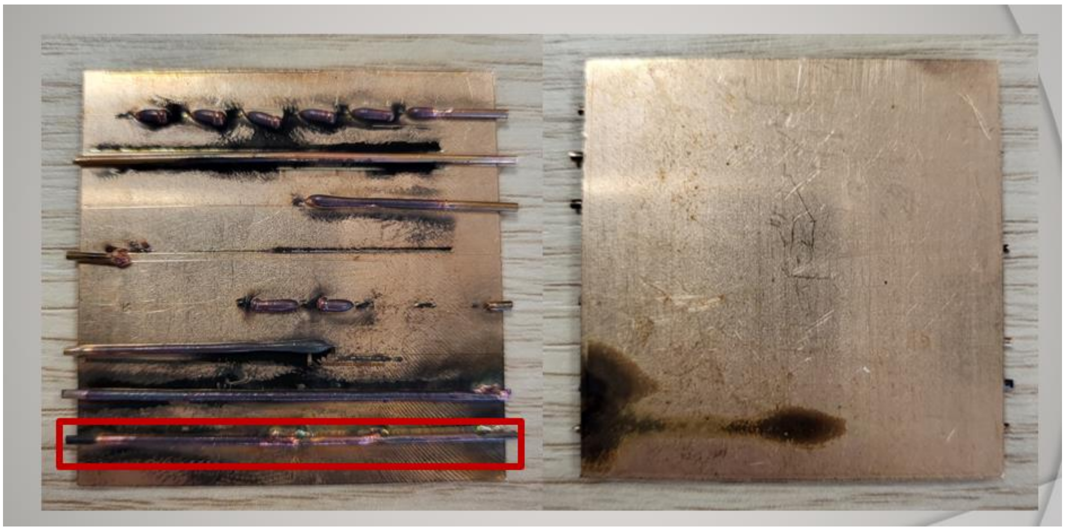

Figure 35: Welding Test

Chapter 6

Conclusions and Recommendations for Future Developments

6.1 Conclusions

Copper and Gold Processing - IR Vs Green Laser

Comparing the process data found in the SoA and those obtained during this study, it is easy to see that the relative density values are clearly better by using a green laser than an IR one, both in the case of copper and gold.

The third column of Table 15 shows the relative density values of copper, using an IR laser, the maximum value obtained is 96 %, while looking at the third column of Table 16it is easy to understand how the relative density values are better using a green laser, values of 99.5 % are reached.

The scanning speed is the same in both cases, however the power used for processing the material changes, in the case of the green laser is lower, this allows to reduce energy consumption.

Table 13: Copper Processing – IR State of Art

Copper Processing - IR state of art		
Power (W)	Speed (mm/s)	Relative Density (%)
750	200	94,5
800	250	95
850	300	95,5
900	350	96
950	400	95,7
1000	450	95,3

Table 14: Copper Processing – Green Laser

Copper Processing - Green laser		
Power (W)	Speed (mm/s)	Relative density (%)
120	200	98
130	250	98,5
140	300	99
150	350	99,5
160	400	99,3
170	450	99,1

The third column of Tables 19 and 20 shows the relative density values for gold, as the power and scanning speed vary. Using an IR laser, the maximum density obtained is equal to 85.5 % while the use of the green laser allows to reach a density of 98.9 %.

The Power used in the case of the green laser are slightly higher, but this allows us to work at very high speed and consequently significantly increase productivity.

Table 15: Gold Processing – IR State of Art

Gold Processing - IR state of art		
Power (W)	Speed (mm/s)	Relative density (%)
40	50	84
45	55	84,5
50	60	85
55	65	85,5
60	70	84,7
65	75	84,2

Table 16: Gold Processing – Green Laser

Copper Processing - Green laser		
Power (W)	Speed (mm/s)	Relative density (%)
130	350	98,1
135	370	98,3
140	400	98,9
145	450	98,7
150	470	98,5
155	500	98,2

Table 21 summarizes the maximum relative density achievable data and the productivity data. It should be noted that the latter increase using a green laser source, both in the case of copper and gold.

Table 17: Productivity and Density Result

	Copper		Gold	
	IR laser	Green laser	IR laser	Green laser
Productivity (cm3/h)	36	43,2	1,87	96
Relative density (%)	96	>99	85	>98

6.2 Recommendations for Future Developments

Some of the potential areas for future work are mentioned below:

- Characterization of the **new material alloy.**
- Copper pure or other copper alloys **process feasibility.**
- Construction of combustion chambers.
- **Geometrical feasibility** with PBF technology.
- Use of **new laser sources** in order to overcome the high reflectance of copper and gold materials.
- Development of component with **specific mechanical properties.**
- **New machineries** for the accommodation of the application and the large dimensions of the components.
- **Parameters optimization.**
- Verification of **thermal** and **electrical conductivity.**
- New development **blue laser.**

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