JEWELRY PRODUCTION BY BINDER JETTING ADDITIVE MANUFACTURING TECHNOLOGY: OUR EXPERIENCE ON STEEL, PLATINUM 950 AND SILVER 925

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INTRODUCTION:
Binder Jetting Technology (BJT) is a type of additive manufacturing process that uses a binder material to selectively bind powder particles together, layer by layer, to form a solid object. This is done by using a special printer whose printheads deposit the binder on a powder layer of controlled thickness, and iteratively depositing a new layer of powder using a roller. The object after printing will undergo sintering with a thermal treatment in order to obtain mechanical strength and high density (example shown in Figure 1).

BJT has characteristics that promise advantages over other additive manufacturing methods, such as high speed, total reusability of the powder inside the machine, high stability during printing and the ability to produce complex geometries with different materials without the use of moulds. This technology can also be used to produce metal parts with very high density and excellent mechanical properties, which makes it suitable for various industrial applications, including jewellery. In this article, we will provide a detailed description of the extensive work we have been doing on BJT in our laboratories in Bressanvido (Italy), focusing on the results obtained with different materials such as steels, silver 925, platinum 950, all alloys used in jewellery making or in the fashion accessories industry.

Figure 1: BJT green part as obtained from printing and curing

The jewellery manufacturing industry is looking for AM technologies as a means to shorten the distance between CAD design of a jewellery item and obtaining the final metal object. However, BJT is still not well-known in the jewellery sector, despite its growing popularity in other metal-making industries. This is the reason why we are investigating the potential and the limitations of BJT for jewellery production. After a discussion over the most relevant parameters for a successful printing and sintering of a BJT item, in the article we will present and discuss the results so far of the use of different alloys, making a technical evaluation concerning relevant parameters such as surface finishing and quality of the items produced.

1. What is Binder Jetting Technology?
Process description

Binder Jetting Technology is an additive manufacturing technology meant to create complex and intricate designs that are difficult or impossible to achieve with traditional methods such as casting, CNC (Computerized Numerical Control) milling, or MIM (Metal Injection Moulding) enabling to produce jewellery items directly from CAD models, without the need for moulds or tooling.[1]

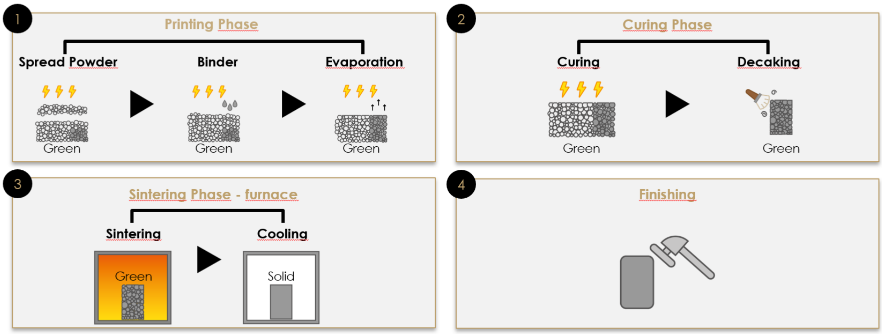

Figure 2: schematics of BJT process

The production of an object by Binder Jetting involves a sequence of several steps, displayed in Figure 2. Starting from a CAD model of the object to be produced, the dimensions are scaled up, in anticipation of the volumetric shrinkages due to the process, and, if needed, supports or dies are created to contain the deformations. A special software, starting from the CAD, performs a slicing of the pieces, obtaining 2D layers superimposed on the 3D models. The material from which it starts is a fine metal powder of controlled size. The most suitable metal powders for this 3D printing process are spherical, to increase the smoothness of the powder bed (and allowing reduced interactions due to sharp edges). The powder is loaded into the tanks of a build unit, i.e. a cart in which the 3D printing process is developed. Inside the printer, a roller spreads a layer of powder in the build unit of predefined thickness. Subsequently, the print heads apply a binder, selectively, according to the 2D images previously obtained; these two steps are repeated until the complete height of the objects to be produced is reached. To avoid saturation, i.e.: excessive and irregular deposition of the compound, the binder is applied in multiple passes on the same layer. In the first passes a smaller quantity is applied, with primer function and in the following ones, with binder function on a larger quantity. The only dimensional constraints to the printing process are the dimensions of the operating area of the build unit and the printing time is determined based on the number of layers to be spread, that is, based on the height of the objects to be printed (Figure 3). Consequently, more objects can also be produced on the same platform, and more layers of objects can be printed.[2]

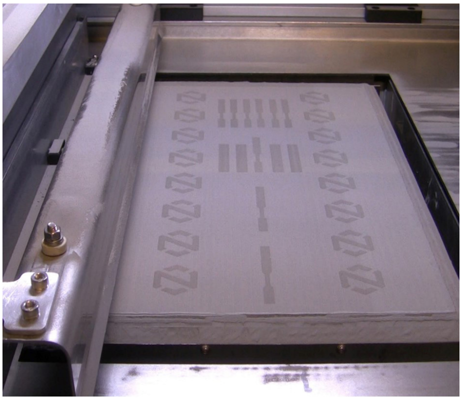

Figure 3: printing phase, binder being selectively deposited over a powder layer

To obtain solid, mechanically resistant semifinished parts, however, a curing phase is necessary to solidify the binder and extract the excess solvent.

The build unit is therefore placed in a curing station where a curing treatment takes place between 120°C and 180°C, depending on the material sensitivity: the binder, consisting essentially of a polymer resin, cross-links and the "green" objects are obtained, solid but still fragile, immersed in a bed of powder; after an accurate decaking (i.e.: extraction of the items from the powder bed) and depowdering process (meant to eliminate excess of powder on the surface), the greens are placed in the sintering furnace.

In the furnace an appropriate thermal cycle is carried out in three phases:
1. Debinding: the binder completely sublimes, inside the furnace the objects are made up only of unbound powder grains. The temperature in this phase is determined by the type of binder and the possible interactions between necking and extraction. The treatment time is determined by the geometry of the pieces and the interactions between powder and binder.
2. Sintering: The particles begin to coalesce and a metallurgical bond is formed; in this phase most of the volumetric shrinkage of the process occurs. The temperature and time are determined by the type of material, whereas adjustments can however be made based on the geometries of the pieces to be treated.
3. Cooling: objects cooling is controlled to avoid residual stresses and unwanted cracks, but also possible metallurgical phenomena or unwanted precipitations due to too fast or too slow cooling. The ramp is structured according to the geometry and mass distribution of the objects.

After cooling, the items are ready to be finished in fashions similar to decorative objects produced with other techniques.

Other competitive AM and traditional technologies

Metal Injection Moulding (MIM)

The MIM process (Metal Injection Moulding) is the direct competitor of binder jetting, of which it is a precursor and with which it shares the same sintering process. The substantial difference lies in the generation of the green: MIM is not a 3D printing process starting from CAD. In MIM, the powder is pre-mixed with a relevant quantity of polymer that acts as a binder. The feedstock so obtained is then injected into a mould, where the curing phase takes place. There is no exchange of information between the operating machine and the 3D design software.[3]

Compared to BJT, the main advantages of MIM are a better dimensional control of the objects and an improved final surface quality, as the greens are in contact with a polished metal mould and not directly with the powder bed. However, MIM works with a mould that imposes geometric constraints on the final shape of the item. The production of the mould, usually manufactured by subtractive technologies is a demanding and time-consuming process, with high costs (depending on size, complexity of pieces to be extracted) that are justified only with a very high number of items produced. This is generally unfeasible with jewellery production, where batches are usually very small compared to industrial productions, and where the creativity and complexity of the designs may offer several challenges to extraction of pieces from a mould, due to undercuts or hollow geometries for example.

Powder bed technologies: Selective Laser Melting (SLM) and Electron Beam Melting (EBM)

Production with Selective Laser Melting (SLM) or Electron Beam Melting (EBM), unlike MIM and BJT, do not go through a shaping and sintering of the objects, but directly produce the finished piece by local melting of the powder bed. In Selective Laser Melting, or Powder Bed Laser Fusion, the powder bed is laid in layers of 30 µm to 70 µm in a similar way to BJT printing. A laser beam, directed and focused, provides the energy needed to melt the powder. The laser selectively points to the areas occupied by the section of the object, based on a slicing of the 3D CAD design in a similar way to what happens in BJT, causing the fusion, and consequent resolidification, of the powder as a solid surface. The process takes place in a controlled atmosphere, protected by Argon, to avoid the formation of oxides and inclusions.[4]

The EBM process also consists of selective melting, layer by layer, of the powder bed. The melting in this case is generated by a high-energy electron beam. To improve the precision and avoid deviations of the beam, it is necessary to operate in vacuum for this procedure. Moreover, to limit the thermal gradient, the powder bed is pre-heated.[5]

After both processes, the powder bed is removed by suction and the pieces must be mechanically separated from the base on which they grow. The advantage of these technologies is that the objects are made in a single step, directly from CAD drawing and the achievable dimensions, not having to undergo sintering processes, can be comparatively larger. On the other hand, the processes operate much more slowly than BJT printing and also, given the strong thermal gradients that are generated in the process, the objects usually have very high internal residual stresses. Concerning surface quality, SLM offers items with high density, but the surface roughness of an item produced with this technique is comparatively high, leading to high loss in case of precious metals working. Another source of loss to this concern is the need to work with an extensive amount of supports that are used during the building of items and that have to be scrapped after construction.

Investment casting

Investment casting is one of the best known production processes in the world of jewellery, having proven over time to be particularly suitable for the production of precious alloys, as it allows to obtain objects of high quality, detail and precision. Investment casting also allows to create complex objects, with intricate or thin geometries. The process involves the production of metal objects using the lost wax technique, which consists of creating a model in wax or in another sacrificial material such as a resin (as it happens for rapid prototyping) of the desired object, which is then covered inside a flask of refractory material. The flask is heated to melt and expel the wax, leaving a cavity in the shape of the object. Subsequently, the flask is filled with molten metal, which takes the shape of the object after cooling. The flask is then destroyed to extract the finished object.

Additive Manufacturing has long become a part of the investment casting process, through the aid of resins or waxes that can be printed using 3D printers, and that have the main advantage of obtaining directly from CAD the item to be cast, no longer needing the production of wax objects by means of rubber molds: in addition to shortening the number of process steps, there is also an advantage from the point of view of the type of obtainable pieces, with thinner thicknesses and more complex shapes, which would not be feasible due to undercutting or lack of mechanical resistance of the wax piece.

Although extensively available in the sector of jewellery, it should be noted that casting remains a very empirical process, complex to control in all aspects, and in which the achievement of an acceptable final result often passes through many casting attempts with considerable consumption of metal and time. Another relevant negative aspect is that of environmental impact, mainly due to the consumption of large quantities of refractory material that is not reusable and has to be disposed, and the production of fumes from the combustion of waxes and resins.

Computer Numerical Control (CNC)
CNC stands for Computer Numerical Control, and it is a subtractive technology that allows the creation of metal objects with high precision and accuracy. CNC machines use computer-controlled tools to cut, drill, mill, or turn metal blocks into desired shapes and sizes. CNC technology is widely used in the watchmaking industry, as it enables the production of complex and intricate parts, such as cases, bezels, dials, movements and any other parts that require high precision in shapes and dimensional tolerances. CNC technology is today relevant in the watchmaking industry and in part of the jewellery making industry, although with low speed of production per single piece, and with a high consumption of material, which is chipped, stained with oil and has to be scrapped or only partially reused.

Other techniques
Just to mention, traditionally jewellery production is also associated to mechanical deformation techniques where the use of mechanical force alters the shape and size of metal sheets or wires. Some common examples of these techniques are stamping and chain making. Stamping and blanking are processes that use dies and punches to create patterns, shapes, or holes on metal sheets. These can be done by hand or by machine, and they can produce various designs and effects, such as textures, reliefs, or cut-outs. Stamping can also be used to make components for other jewellery pieces, such as clasps, links, or charms.

Chain making is a process that involves bending, twisting, or linking metal wires to form chains of different styles and lengths. Chain making can be done by hand or by machine, and it can produce various types of chains, such as cable, curb, rope, or snake. Chain making can also be combined with other techniques, such as soldering, weaving, or plating, to create more complex and decorative chains.

Traditional mechanical deformation techniques offer in some cases a fairly inexpensive (from the point of view of tools and plant needs) possibility to obtain a wide variety of designs with very low thicknesses and high surface to volume ratios, that at the moment may still prove challenging to achieve with AM technologies. With that said, they represent a more craftmanship oriented approach towards the production, with limited possibility to reduce manual work and automatized processing.

Metal sintering theory

Under the generic word "sintering" an array of different processes can be mentioned. Although in all cases solid bodies are obtained thanks to the coalescence of particles that were originally separate, sintering can be divided into different types based on the driving force, the atmosphere, the temperature, the pressure, and the heating method.

Sintering, as referred to the process needed in Binder Jetting Technology, is a process of fusing metal particles together by heating them without external overpressure to a temperature below their melting point, creating a solid mass. The sintering mechanism involves the movement of atoms across the particle boundaries, which lowers the surface energy and porosity of the system.[6] Sintering should achieve maximum density, and in general allow the creation of complex shapes and structures with high superficial quality and homogeneous mechanical properties.

Unlike some other sintering methods, such as hot isostatic pressing or spark plasma sintering, binder jetting technology does not require any pressure to achieve sintering. The process works at environmental pressure, which reduces the cost and complexity of the equipment and allows for larger parts to be sintered. However, this also means that higher temperatures and longer times are needed to reach the desired densification, which can affect the microstructure and properties of the sintered materials.

Sintering as of BJT specifications occurs in solid phase; the presence of liquid phase is to be avoided due to the risk of distortions of shape modification, as the items are not held inside moulds but are sintering on trays in a controlled atmosphere furnace.[7] The driving force of the process is the reduction of the surface energy in favor of the volume energy. During the formation of solids, starting from ideally spherical particles, the total free energy (ΔG_T)

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is given by the contribution of two factors: volume free energy, dependent on the third power of the particle radius, and surface energy, dependent on the second power of the particle radius:

$$\Delta G_T = 4/3\pi r^3 \Delta G_v + 4\pi r^2 \gamma$$

where r is the particle radius, ΔG_v is the volume free energy and γ is the surface tension. As can also be seen from the graph in Figure 4, for stable nuclei of radius greater than the critical radius, a condition of greater stability is given by the growth of particles.

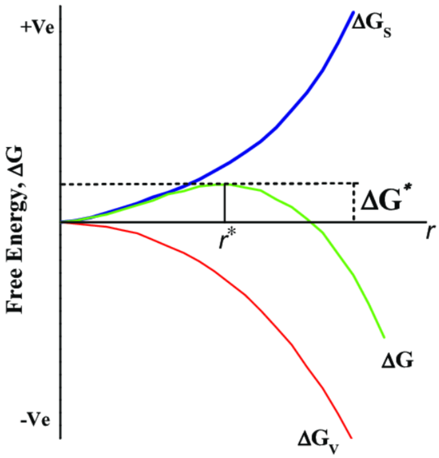

Figure 4: total free energy of a powder particle as a function of volume and surface free energies

Additionally, taking into account the Laplace law for spherical surfaces:

$$\Delta p = 2\gamma/r$$

where Δp is the pressure difference on the interface (exterior pressure minus interior pressure), one can notice that as the radius of the particles increases, the pressure difference on the outer surface of the forming particle decreases. Considering the two phenomena mentioned above, at sufficiently high temperatures, close to the melting temperature, which favor the diffusive phenomena of material transport between several particles, a state of greater stability is reached with particle growth.

Several mechanisms contribute to sintering: diffusion inside the material, on the surface and evaporation/condensation mechanisms, as can be seen in figure 5.[8] The phenomena of evaporation, condensation and transport along the surface contribute only to the grain growth, while the phenomena of diffusion from the core of the particles contribute to the densification of the parts.

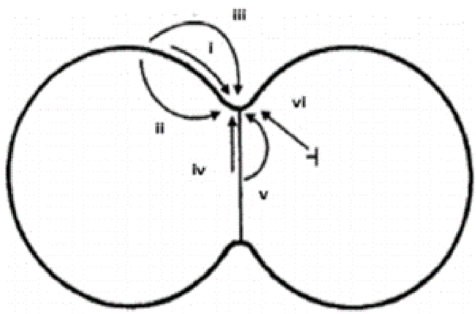

Figure 5: mechanisms contributing to the necking and densification of powders during sintering

1. **Surface diffusion**: This mechanism involves the transfer of atoms from the surface of one particle to another along the neck that connects them. The driving force is the reduction of the surface energy, which is higher at the curved regions. Surface diffusion does not change the shape of the particles, but only increases the size of the neck.
2. **Lattice diffusion** (superficial): This mechanism involves the diffusion of atoms from the surface of a particle into the bulk of another particle through the surface layer. The driving force is the concentration gradient between the surface and the interior of the particles.
3. **Vapour transportation**: This mechanism involves the evaporation of atoms from the surface of a particle and the condensation of atoms on the surface of another particle. The driving force is the difference in the vapour pressure between the particles, which depends on the curvature of the surface.
4. **Grain boundary diffusion**: This mechanism involves the diffusion of atoms along the grain boundaries between the particles. The driving force is the reduction of the grain boundary energy, which is higher than the lattice energy. Grain boundary diffusion brings the particle centers closer together, resulting in densification and shrinkage of the material.
5. **Lattice diffusion** (from grain boundary): This mechanism involves the diffusion of atoms from the core of a particle to the grain boundary and then to another particle. The driving force is the difference in the chemical potential between the particles, which depends on the curvature of the surface and the pore pressure.
6. **Plastic flow** (from dislocation motion): This mechanism in-

volves the deformation of the particles due to the movement of dislocations under an applied stress. The driving force is the reduction of the elastic energy stored in the particles.

Therefore, mechanisms 1, 2, and 3 do not bring the centers of the particles closer together, but only affect the surface area and the shape of the particles. Mechanisms 4, 5, and 6 densify the material, displacing matter from the grain boundaries and reducing the porosity and the volume of the material.

2. Operation sequence and key parameters of BJT

CAD file design

To design a part that will be printed with the Binder Jet Technology, it is necessary to take into account some specific aspects, such as:
- Geometry: the part preferably should a shape suitable for the printing technique, being aware of the complexity of managing acute angles, sharp edges or difference in size of walls that could cause problems of thermal distortion, issues that become visible after sintering. In addition, and more importantly, a scale factor must be defined for the design of the part that takes into account the shrinkage that will occur at the same time as the binder evacuation and sintering.[9] In our experience, we described the complexity of an item as "simple", "medium", "hard" on the base on factors like size, planes of development, details complexity, geometrical tolerances and so no. The simplest objects to print have for example a planar development and a size less than that of a credit card. An item with larger size, three dimensional development and a filigree over the surface may be considered as "hard".

- Supports: in case the item is thought to undergo a non-homogeneous distortion, it helps to design supports that can be co-printed and will shrink with the exact same pattern as the item to printed, thus avoiding undesired geometrical variations. An example of a support to guarantee circularity on a watchcase is shown in figure 6.

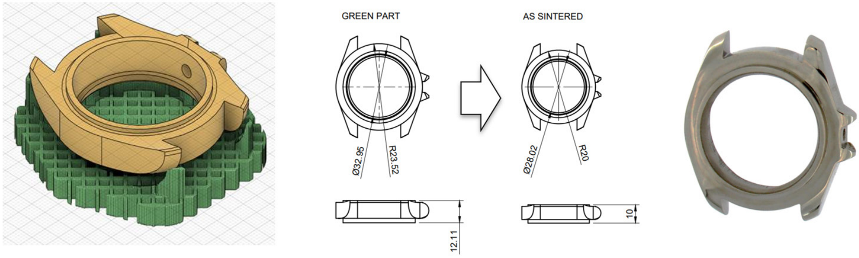

Figure 6: CAD design of a watchcase as studied for BJT processing with support to avoid geometrical distortions

- Orientation: the part must be oriented in such a way as to minimize the necessary support and the amount of material used, optimizing the printing times and costs. The orientation also affects the direction of the residual stresses and the distribution of pores in the part, which can influence the mechanical and physical properties of the finished part.

- Hollowing: with the correct designing, a part can be hollowed out internally to reduce the weight, the material consumption and the printing times. The hollowing out must be done in such a way as to maintain a good mechanical strength of the part and to facilitate the removal of the excess powder after the printing. It is possible to create outlets or internal ribs to ensure these requirements.

Printers

Ideally any BJT printer model can be chosen to print as the interaction during printing between binder and powder particles does not create difficulties in terms of material to be printed, as long as the correct particle size is chosen in relationship with the resolution needed. However, we dealt with two main categories of materials: precious metals, such as platinum 950 and silver 925, and non-precious metals, such as steel and bronze. Precious metals require a high level of control for what concerns loss of metal powder and, understandably, a low amount of powder actually inside the machine due to costs: for the latter reason, it is important to choose a printer with a comparatively small size platform. For non-precious metals one can allow higher platform size to maximize productivity and likely operations on larger size items. To accommodate these different needs, we have selected two types of printers.

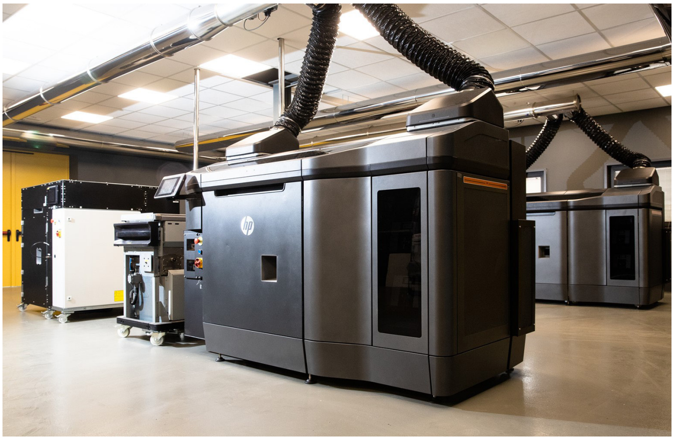

Figure 7 (left to right): curing station, build unit and main printer unit (HP MetalJet S100)

For steels, bronze and silver, we have been using since the beginning of the project in 2022 two HP MetalJet S100 printers (Figure 7), which can handle these materials on a platform of 430 mm x 310 mm x 140 mm size. This leads to 18,7 dm3 volume, enough to handle 200 kg of steel and 250 kg of silver 925 at full load on the machine.

At a later stage, a smaller unit from Desktop Metal (P1) was added to the operations, which proved suitable for silver 925 and platinum 950 and operates on a 200 mm x 100 mm x 40 mm platform, a volume of 0,8 dm3 and a full load of 30 kg of platinum powder or 20 kg of silver 925.

These printers have several characteristics in common, such as the use of metal powders and binders (each with proprietary formulations), the layer-by-layer printing process, and the post-processing steps of curing and sintering. However, they also have some unique peculiarities, such as the printing speed, the binder jetting technology, the powder distribution system, and the curing and sintering parameters.

The learning curve on understanding and optimizing the use of each printer is a result of the interaction of several aspects, strengths and weaknesses deriving from the kind of metal used, the printer, the sintering furnace and several other fine details.

Printing framework
We use the definition “printing framework” to describe the list of parameters that can be modified to optimize the printing, where five areas of main interest are highlighted:

The first area enables to apply dimensional compensations due to thermal phenomena along the three axes in case of dimensional variations after printing and curing compared to the original CAD model.

The second area of parameters concerns the level of binder, defined as "contone". There is the possibility to adjust both the total amount of binder per printing layer, and the distribution of the binder for each pass, since four passes of binder are distributed for each layer. Dividing the amount of binder deposited on each passage allows for a more homogeneous deposition, resulting in a smoother powder distribution and sintering results.

The third category concerns the core-shell function. This function allows to intervene when there are differences in density between the inner part, the core of the object, and the outer part, the "shell". Here one can adjust the saturation of the binder within the two zones, determine the thickness of the skin and the thickness of the transition zone, where the machine will automatically scale the amount of binder to go from one zone to another.[10,11]

The fourth category concerns the actual technical parameters of printing: the printing temperature, the rotation and translation speeds of the powder spreading roller and the amount of powder supplied per pass, determined by the rise per pass from the side tanks.

Finally, one can define parameters related to the curing phase, in particular the curing temperature and time, in the form of three coefficients.

Curing and decaking

The printed objects are very fragile before curing, as they consist of loose powder particles held together by a thin layer of binder. If they were extracted from the powder bed at this stage, they would break or deform easily. Therefore, they have to undergo a curing phase, in which the binder is heated and polymerized, forming stronger bonds between the particles and creating more solid "green" objects that can be handled and removed from the powder bed without damage.

Cross-linking for the binder occurs when thermally treated between 120°C and 180°C, depending on how sensitive the material is: the "green" objects are formed, solid but still delicate, inside a powder bed; after a careful process of removing the excess powder and cake, the greens go into the sintering oven. Items at this stage have an ultimate tensile strength in the range of 10-15 MPa.

Here follows one of the challenges of BJT: the extraction of the cured objects from the powder bed. This is a very time-consuming and manual work, as the excess powder needs to be carefully removed with brushes, air blowers, or vacuum cleaners, without damaging the delicate structures. However, the powder, once scraped off from the pieces, can be reused as it is clean from polymer residues and from our experience can be worked again without issues or need for pre-processing it. The fact that virtually all the powder available in the powder bed can be reused to work further pieces makes BJT a valuable technique from the point of view of sustainability and metal loss, as there is no powder to be scrapped or wasted during the process. The powder can be reused multiple times without affecting its quality or performance, reducing the costs and environmental impact of the production.

Debinding and sintering process

Debinding, i.e. the elimination of polymeric compounds used to link together the metal powder particles before sintering occurs is operated in BJT in a simpler fashion than it is for MIM, where the amount of polymer contained in the feedstock to have the mixture be injected is much higher and demands a first step of catalytic debinding in which the green items are treated by being attacked by catalytic acids vapors, usually nitric acid, with evolution of large amount of scraps and chemical byproducts. BJT works with a much lower amount of binder (3-4% in BJT as opposed to up to 40% in MIM), that enables to get it disposed simply with a thermal process as an initial step of the sintering.[3]

The sintering process of the green parts takes place in special furnaces that act in a controlled atmosphere, with inert (Ar or N_2) or reducing (H2) gas or a mixture of them (figure 8). The furnaces used in our facilities are semi-automatic electric furnaces with metal chamber, with tungsten resistances and shelves in molybdenum that can reach temperatures up to 2000°C.

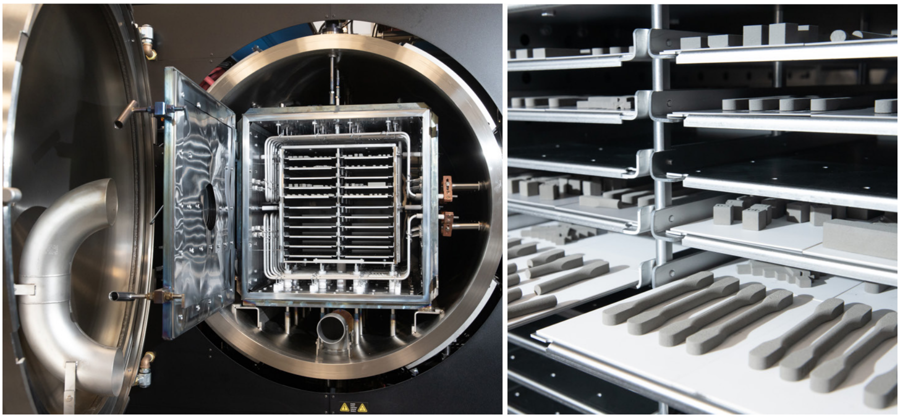

Figure 8: Furnace used for sintering steel items, and detail of alumina trays holding samples

In order to ensure a high quality of the treatment and a high purity of the gases, the furnaces are equipped with vacuum pump and precision regulators for the gas flow. For the treatment with pure hydrogen or mixtures of it, there is also a torch for the treatment of the exhaust gases and an emergency inert gas tank. All the process data are recorded to allow a subsequent analysis of the treatments. In Figure 9 a typical cycle for sintering an AISI316L steel alloy is presented.

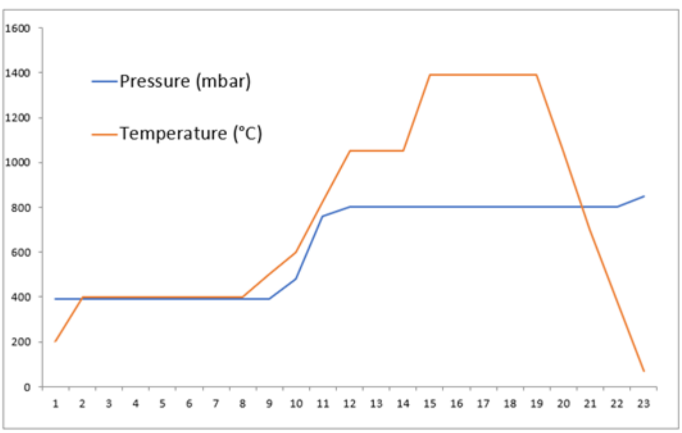

Figure 9: sintering cycle for BJT AISI316L, as pressure / temperature against time (h)

The lower temperature plateau zone at approximately 400°C and 400 mbar pressure is where debinding occurs, with conditions that are allowing efficient evaporation of polymers, occurring in a range between 400 and 420°C and enough time (6 to 8 h, depending on the thickness of the item) to eliminate all possible organic residues that would hinder the metal to achieve full density during sintering.

A steep increase in temperature (from 400°C to 1100°C and further on to 1400°C for AISI316L) marks the actual beginning of sintering phase, where it is also advisable to operate a short pre-sintering phase (1100°C for a couple of hours in this case) that reduces the risk for mechanical distortions before moving to densification.

The sintering cycle described above is suitable for AISI 316L steel, but not for other materials, such as Ag925, Pt950, or even different types of steels. Each material has its own optimal sintering conditions, depending on factors such as the melting point, oxidation resistance, and alloy composition of the metal powder. Moreover, the interaction between the metal particles and the binder at low temperatures can affect the debinding process and the quality of the final product. Therefore, it is necessary to adjust the sintering cycle parameters, such as temperature, duration, and heating rate, according to the specific characteristics of each material and the desired properties of the sintered item.

3. Experimental activity

We selected formulations with diverse properties and applications: AISI316L, PANACEA and 17-4PH steels, Ag 925 silver, bronze, and platinum 950. These alloys are widely employed for industrial and jewellery purposes, and exhibit different melting points, hardness. We fabricated analogous parts with each material using Binder Jetting Technology, and then conducted an extensive characterization of the resulting products.

Considering that the presence of defects in terms of porosity/lacking density is distributed evenly in the volume of the item, it is possible to identify systems for qualifying a sintering cycle on the base of standard pieces (first tests where performed on items as shown in Figure 10): this allows to standardize the kind of performance expected on items that would be more difficult to handle or more powder consuming.

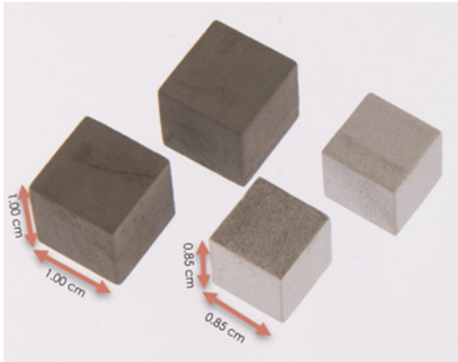

Figure 10: standard cubic sample used for sintering performance evalutation

The array of parameters we considered to assess a quality evaluation over the pieces involves:

Surface roughness of as sintered pieces: this is a parameter of obvious relevance for the work needed after sintering in terms of finishing, with an indirect indication over the loss expected over a production. Measures were carried out with a Keyence VHX-7000 image processing software according to ISO21920-2:2021 standard (example as shown in Figure 11).

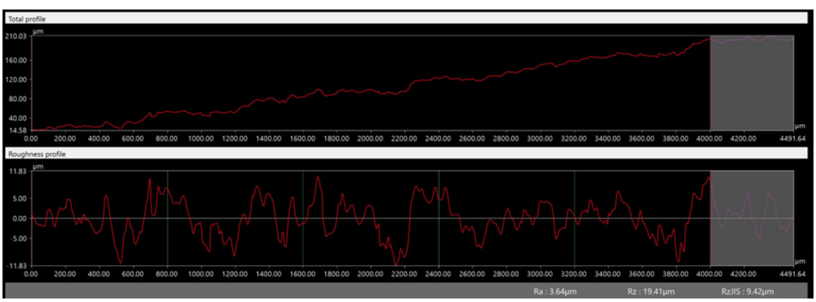

Figure 11: roughness measurement examples on sintered pieces

Residual porosity: this value is obtained as a percentage by preparing a cross section on an item, followed by image analysis to gather information on the percentage of area that is not densified. According to our experience, measuring the presence of porosities in a cross section is a viable method to predict the amount of superficial porosities that can be seen after polishing. Cubes of 10 mm size were chosen as the first testing items. Pieces were metallographically prepared on three faces (xy plane, xz plane, yz plane), indicative of the different printing and sintering directions of the object. From the surface of the object, 0.3 mm were removed by abrasive papers, followed by metallographic polishing. The measurements of residual porosity, average and maximum pore size were carried out with a Keyence VHX-7000 image processing software according to internal operating procedure.

Geometric deviations: this parameter is heavily dependent on the shape of the item, the presence of undercuts, supports and mass variations in different areas of the item. It is calculated by measuring with precision devices the final item after sintering and comparing it with the original CAD design before the corrections needed in printing.

Mechanical properties: hardness measures on the fabricated parts also considering the impact of post-processing methods such as heat treatment and polishing. Here, metallographic cross sections were analysed using a microhardness tester QNess Q10A+ 200 g load, 15'' time.

Microstructure/phase composition: standard metallographic investigations were performed on items of certain interest.

Carbon content: measure over carbon content is an indirect indication over the amount of carbon residue (unevacuated binder) trapped in the microstructure. This is a relevant measure for items that underwent incomplete or improper sintering, and completes the information offered by residual porosity measurement. Carbon content measures were done using an ELTRA ELEMENTRAC CS-i C/S analyzer according to ASTM E1019:2018 standard.

Results

The following section presents the results in more detail, with the table below illustrating the main findings and relevant characteristics of the alloys chosen.

Table 1: summary of charactization data on the alloys tested

Characteristics	AISI316L	PANACEA	17-4PH	Ag925	Pt950
Roughness Ra (µm)	3.0-3.5	3.5	3.0-3.5	3.0-3.5	3.0-3.5
Roughness Rz (µm)	15	15	15	15	15
Residual porosity (%)	0.2	0.3	0.4	0.9	0.4
Average pore size (µm)	6	6	6	6	3
Maximum pore size (µm)	30	35	35	60	25
As sintered hardness (HV02)	130	250	300	50	150
Particle size (µm)	d10: 5 d90: 22	d10: 5 d90: 22	d10: 5 d90: 22	d10: 7 d90: 28	d10: 4 d90: 25
Sintering window (°C)	1350-1390	1260-1300	1270-1310	810-830	1750-1760

AISI316L steel

AISI 316L is an austenitic stainless steel alloy that has been widely used in the additive manufacturing industry since its inception. It is suitable for applications that require high corrosion resistance, such as investment casting and jewellery making.[12] It is also the formulation on which the whole startup of BJT plant was performed; the learning curve took approximately half an year (March/October 2022) starting from first prints all the way to satisfactory, stable sintering cycles on common use items for jewellery.

AISI 316L has been tested on various printers and furnaces, and has proven, after fine tuning, to be compatible with different process parameters and post-processing treatments. We may consider it today as the benchmark material for our Binder Jetting applications, and currently it is being used as a testing formulation for items of larger size, where distortions and geometric deformation issues are more challenging.

PANACEA steel

PANACEA steel (acronym for Protection Against Nickel Allergy, Corrosion, Erosion and Abrasion) is a high-hardness nickel-free steel that has been developed for the fashion industry, where it is used for making accessories such as watches, bracelets, and earrings. It can be polished to a bright mirror finish and does not cause allergic reactions. However, PANACEA also poses some challenges for the additive manufacturing process, as it requires complex post-nitriding processes to stabilize it against corrosion[13].

To prevent corrosion on a ferritic phase caused by long quenching times (typical of standard sintering cycles), PANACEA needs to undergo nitriding, which is a surface treatment that introduces nitrogen atoms into the metal lattice and forms a protective layer of nitrides.

The nitriding process for PANACEA involves several steps. First, the parts are debound in hydrogen up to 1150°C, which removes the organic binder and reduces the oxygen content. Then, the parts are sintered at 1300°C, which is sufficient to densify them successfully. However, under slow cooling after sintering, PANACEA tends to form a ferritic phase with very poor corrosion resistance. Therefore, to strengthen the chemical resistance, the parts are maintained during sintering in nitrogen, which prevents the formation of ferrite and promotes the formation of martensite and nitrides. Finally, to completely eliminate corrosion, the parts are tempered in nitrogen at 1100°C for 2 hours, followed by fast cooling. This treatment enhances the diffusion of nitrogen and the growth of the nitride layer, resulting in a uniform and dense surface.

Post processing by nitriding PANACEA is effective, but also costly and time-consuming. Moreover, it requires specialized equipment and expertise, which may not be available to all users of binder jetting technology. Therefore, further internal heat treatments are being studied to verify whether nitriding can be avoided or simplified, without compromising the corrosion resistance and the aesthetic quality of PANACEA.[14]

17-4PH steel

17-4PH is another type of stainless steel that can be used for binder jetting technology, especially for the production of mechanical tools that require high strength and hardness. Unlike PANACEA, which is Ni-free, 17-4PH is a nickel-based martensitic steel, which means it contains about 15% of nickel as an alloying element. Nickel increases the corrosion resistance and the toughness of this steel, which is also magnetic, that may be a desirable or undesirable property depending on the application[15].

One of the advantages of 17-4PH is that it has high mechanical properties, such as yield strength, tensile strength, and hardness, even in the as-sintered condition. 17-4PH is also a markedly hardenable steel, which can be tailored to different levels of performance and durability.

Among the powders used so far for binder jetting technology, 17-4PH is the only one that is water atomized, rather than gas atomized. Water atomization is a process that uses high-pressure water jets to break up molten metal into fine droplets, which then solidify into spherical particles. This method is cheaper and faster than gas atomization, which uses inert gas instead of water. However, water atomization also leads to some differences in the sintering behavior of the powder, compared to gas atomized powders. For example, 17-4PH powder has slightly different sintering scale factors, which are the ratios of the final dimensions of the part to the initial dimensions of the green part. In particular, 17-4PH powder shows a more marked drop in the z axis, which is perpendicular to the build platform, due to gravity and shrinkage effects. This means that the parts printed with 17-4PH may need higher dimensional accuracy and compensation factors than those printed with other powders.

Silver 925

Silver 925 is the first traditional jewellery alloy that we worked on: the first tests were done using a Sterling silver 925 (i.e.: mixture of 92.5% silver and 7.5% copper). Silver 925 posed some challenges for thermally activated sintering technologies, like MIM and BJT, due to its thermal properties and its tendency to oxidize.

A major challenge in working with silver 925 regarded the juxtaposition of the necking temperature for the powder, lower than 400°C for the particles suitable for BJT, and the evaporation temperature of binder, that on the available formulations is in the range of 400-420°C. This leads to the risk of binder residues trapped in porosities that close before being completely evacuated, which is a cause for residual porosity, apart from possible oxidation and contaminations.

To overcome these challenges, we have developed a proprietary alloy that is based on silver 925, but has improved performance for sintering in BJT. The work focused on making the alloy more suitable for sintering without compromising its aesthetic qualities. Additionally, we have optimized the printing parameters to reduce the amount of binder used, and have fine-tuned the debinding and sintering thermal cycles to use different atmospheres that increase the evacuation and evaporation of binder from the green parts under sintering.

The results obtained with the new formulation are very promising, as we have achieved high average densification (above 99,1%) and excellent surface quality on some objects finished by partner companies (example in Figure 12).

This happened to be a somewhat subjective aspect, though: together with some testing companies that are already satisfied with the results after their standard polishing process (and especially on pieces with fairly low maximum size of pores, which makes defects less apparent), there were others that reported extra time for finishing the objects to a satisfactory level.

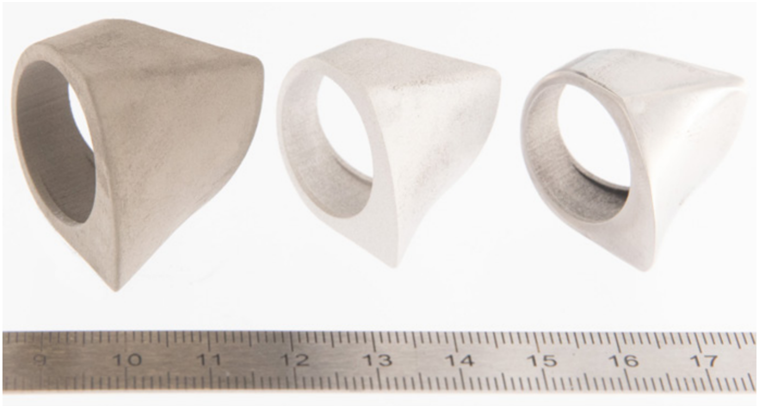

Figure 12 (left to right): green, as sintered, polished pieces in silver 925

The results obtained with our proprietary silver alloy are very promising, as we have achieved high average densification (above 99,1%) and excellent surface quality on some objects finished by partner companies.

Platinum 950

Platinum 950 is the second precious metal that we have tested for BJT printing, as it has the optimal conditions for this process: high sintering temperature, no low-temperature necking, and no powder oxidation in the intermediate stages. We have developed a proprietary Platinum 950 Ruthenium based formulation, which offers a high melting point, high whiteness, and improving densification in comparison with Pt950Co alloy used in conventional casting (and of course, being a Co-free formulation). Moreover, we could use an air furnace sintering, which is simpler and allows the use for simpler furnaces without argon or hydrogen management, without affecting the quality of the final product (example in Figure 13).

Previous tests from scientific literature using platinum 950 showed BJT printing can produce parts with smaller particle size powders (0-20 µm); the work done on optimization of printing and sintering allowed us to start using a powder with a slightly larger particle size distribution, as seen in Table 1, with increased yield from atomization process and comparatively lower cost on the printer feedstock.

Figure 13: green and as sintered wedding bands in platinum 950 alloy produced by BJT

4. Comments and conclusions

On the base of the result done so far, we consider that the results obtained on all high-melt alloys, such as steels and platinum 950, are technically sound and acceptable in particular for what concerns surface quality and results stability on items that are compatible with jewellery, watchmaking and fashion sectors demands. Platinum 950 in particular had the shortest and most successful learning curve, most likely thanks to the previous large experience (and trials/errors sessions!) had with steels. The remarkable result of a residual porosity below 0.4% on platinum 950 was achieved in a matter of few sintering cycles, where the tuning of previous alloys, like for example PANACEA steel, requested a far larger number of iterations due to a more complex array of characteristics of the alloy, not to mention the need to improve corrosion resistance.

In concerns to surface roughness, the average values obtained are dependent on the layer thickness and the powder size distribution used rather, than on the alloy: although rougher than on as cast pieces from investment casting (which may be considered as the benchmark for roughness quality, usually with Ra below 2 µm in as cast conditions), the average Ra value of 3 to 3.5 µm was considered acceptable given the fact that it is from pieces of an AM technology.

For low-melt alloys, such as silver 925, the surface quality obtained through BJT processing is acceptable but still faces some challenges, especially in the debinding stage. In general, the currently commercially available binders are not optimized for alloys whose solidus is below 1200°C and this results in a higher risk of defects such as porosity . HIPping can be used to improve the densification of the final products, but it adds extra cost and complexity to the process.

Future work from the printers manufacturers side should focus on developing new binders and optimizing the parameters for low-melt alloys, as well as exploring the potential of BJT in terms of equipment tailored for jewellery applications, with smaller platforms, closer circuitry over powder management in order to reduce loss.

One of our next goals will be starting the BJT processing on gold 750‰ alloy powders, as well as a continued work on fine tuning of Ag925 and bronze alloys.

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