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Ilaria Forno is a graduate of Materials Engineering from Polytechnic University of Turin. Now she is studying for a PhD in Industrial Production and Design Systems, developing a thesis sponsored by the Consorzio Promoteo regarding the precision casting of precious metals with an analysis of materials and methods.

Powder Metallurgy is a technology that has been widely used for some time in several industrial sectors and has recently aroused considerable interest in gold manufacturing, especially when used in combination with rapid prototyping techniques such as laser sintering.
The ever increasing availability of metal based and non-metal based alloys with advanced features, supplied in powder form, opens the doors to the use of alternative sintering techniques, borrowed from smelting sectors.
This paper, therefore, aims at analysing the various sintering techniques, also in relation to the different materials used, highlighting the advantages and limits.

Sintering: the applicability of the various powder metallurgy techniques in gold manufacturing

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INTRODUCTION

In recent years, the gold manufacturing and fashion accessory sectors have been the focus of growing interest in terms of innovative technologies, borrowed from smelting sectors, which could result in technological advancement and could, in some way, overcome some of the limits that the traditional lost wax casting process imposes. The desire to create items that, both from the geometrical (filigree, hollow objects, every-day items) and the property (density, dimensional tolerance, metallurgical and mechanical properties) points of view were impossible or extremely difficult to make, has urged the sector to face the challenge of entering into the field of mechanical processing, rapid prototyping and powder metallurgy. In addition to these ideas on products, the production method and economic impact should also be taken into account.

In the specific case of powder metallurgy, interest in this technology, typically used in other industrial sectors, comes from general reflections on metallurgy and mechanics (enormous and potential innovation from a compositional and property point of view) and, due to the specific processes described herein, on geometry (complexity of shape and respect of strict dimensional tolerances).

Before going into detail about the various production technologies, a brief examination of the general peculiarities of powder metallurgy is required, highlighting the common characteristics and the differences between press and sintering methods, injection techniques and additive manufacturing approaches.

Powder metallurgy: general characteristics

Powder metallurgy is a method for producing items and metallic details in a solid form using powdered metal materials as the raw material. This set of processes is extremely broad and complex due to the high number of parameters that can lead to different production methods [1]. To be more precise, an initial classification may be made considering the methodology used for creating the shape of the final component. In this way, we can divide the various technologies according to whether they require the free powders to be pressed inside a mould (press and sintering technology), whether they require the injection of a plastic mass of powders and binding materials inside a metal mould (Powder Injection Moulding technologies, borrowed from the plastic industry) or if additive technologies are needed (layer-by-layer technologies or additive manufacturing). The same technologies can also be classified on the basis of the energy sources that lead to the densification of the compact mass as the powders become solid (thermal, laser, capacitor discharge, plasma) or on the basis of the possible need to mix the powder with an alloying element.

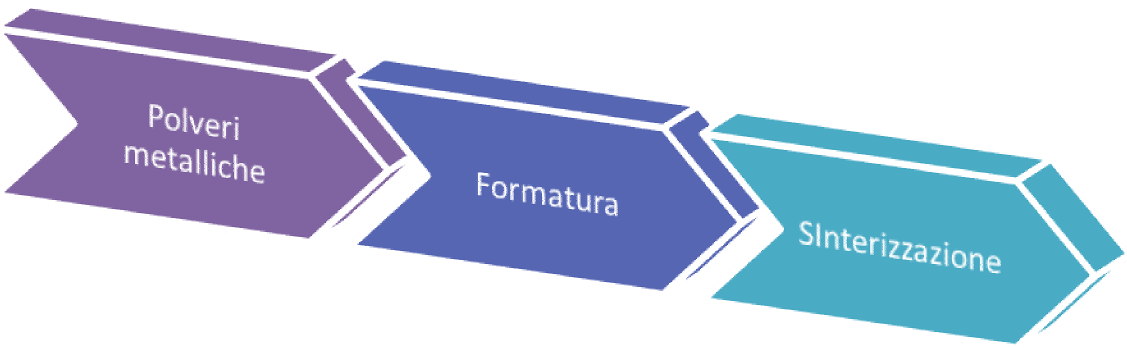

Figure 1 Process phases in Powder Metallurgy technologies

It is evident that the only element that these technologies have in common is that they all use metal powders and a brief description of their general characteristics is therefore necessary.

The production of powders, except in some exceptional cases in which pulverisation from the solid form is performed, is carried out by chemical or electrolytic processes, mainly through a procedure called atomisation. This procedure is conducted starting from the molten metal state. The liquid metal is carefully poured through an opening at the end of which it will be disintegrated and solidified by a water jet (water atomisation) or by a gas flow. The different interaction

between the molten metal and the cooling means determines the peculiarities of the two types of powder, especially from a morphological point of view, since the particles produced by water atomisation will be irregular and spongy while those produced by gas atomisation will be regular and round due to the high pressures involved.
Besides the morphological difference, the powders can also be classified according to the alligation methods. Should an alloy be used, alligation can be performed before atomisation (the molten metal will already contain the binding materials) or, afterwards, in the powder state.
In powder metallurgy, the easiest way to create an alloy is to mix the elementary powders according to a stoichiomentric percentage, in weight, of the binding materials. Apart from the fact that elementary powder mixtures have greater compressibility than pre-alloyed powders, the main advantage of using mixing as an alligation method is that the composition of a blend of powders can be changed or corrected quickly after atomisation. One of the principal disadvantages of this method is that the sintered component is less homogenous and cannot be used in some processes.
Other procedures foresee alligation of the powder particles. This is true of powders pre-alloyed by scattering in which, by means of a thermal treatment, a chemical bond, solidified by diffusive processes, is created between the basic metal powder material and the binding material powders. This will give a base metal particle with the elements of the alloying particles soldered onto the surface in the form of satellites.
Last, but not least, are totally pre-alloyed powders, which are generally obtained by atomisation starting from the molten form of the alloys concerned. Particular properties can be obtained through hybrid systems in which the powders resulting from the various methods are mixed together [2].

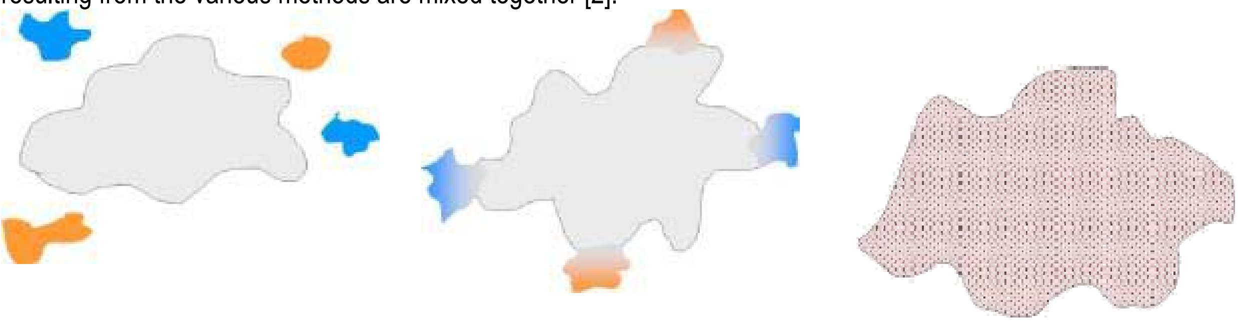

Figure 2 Diagram showing powders mixed mechanically, pre-alloyed by scattering and totally pre-alloyed.

The powder production phase must be followed by a shaping process, or rather, a phase during which the free mass of metal powder should be given a certain geometry. This phase, in the traditional process, is usually performed by using an appropriate geometric mould in which the material is pressed (press & sintering process). This procedure foresees a high number of variants aimed at improving the densification of the material in terms of compressing and isotropy and can include applying heat during pressing or the use of special equipment to allow isostatic pressure to be applied (one example often used is Hot Isostatic Pressing). Pressing processes normally include a thermal sintering phase after pressing, but there are cases in which the two phases are performed simultaneously, taking advantage of the electrical field energy to cause sintering to occur.[3]
Included among the alternative procedures to shaping by compression is injection (Powder Injection Moulding) and additive processes.
Lastly, it would seem appropriate to mention the sintering mechanisms. Traditionally, the sintering process is defined as *"The processing of a powder or a solid compact at a temperature below its melting point with the aim of increasing its resistance by creating bonding between the particles."*
In reality, this definition involves much more than a simple thermal sintering procedure and can be widened to all those technologies that use alternative sintering sources such as lasers, electrical fields or plasma.
In general, the sintering process occurs by transferring mass and the main driving force of the process is the reduction of free surface energy. Thermodynamically, the phenomenon can be explained in terms of surface tension. The particles have curved surfaces that the sintering process tries to eliminate. A high quantity of energy is concentrated onto the surface, which drastically reduces as the curve decreases. Moreover, the steam pressure on concave areas is much less than on the convex ones. During thermal sintering, the densification process, due to the dragging forces described above, is basically conducted according to different mechanisms: scattering (superficial, grain boundary, volumic), plastic flow and evaporation-condensation phenomena.
Parameters, such as sintering time and temperature and the atmosphere in which the process is conducted, play a fundamental role in these procedures.

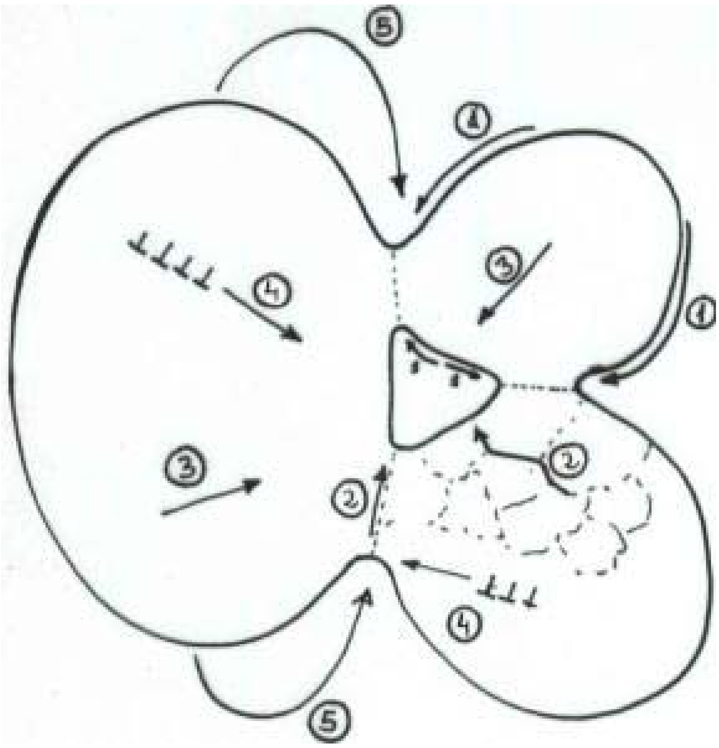

Figure 3 Diagram showing examples of scattering processes: superficial (1), grain boundary (2), volumic (3), plastic flow (4) and evaporation-condensation phenomena (5).

In the technologies using electrical fields, the experimental conditions turned out to be more complex and therefore lead to the consideration that more complex mechanisms may be involved. The nature of these mechanisms is, however, still an item of debate. To be more precise, sintering is due to:

- arc discharge
- electro-migration
- diffusion induced by electrical field
- temperature gradients
- pressure load gradient
- modification of defect concentration

By means of these different processes, free powders tend to form unification zones (sintering necks) that increase until the inter-particle porosity is reduced and densification is therefore achieved [4].

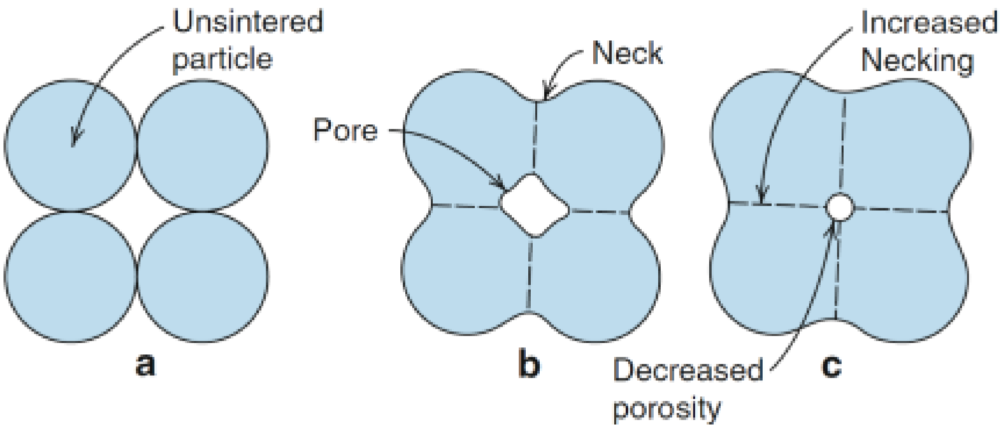

Figure 4 Sintering process of free particles (a), formation of sintering necks (b) and densification (c).

PRESS AND SINTERING TECHNOLOGIES
Thermal press and sintering technologies are largely used to produce a vast number of metal components, whose shape, from a geometrical point of view, is mainly axial-symmetric. These extruded solids can substantially be classified into two categories:

1. Components that are difficult to produce with other methods, for example, details made in tungsten, molybdenum or tungsten carbide. Additionally, porous spheres, filters, composite materials and many other types of soft or hard magnetic components that can only be made by PM.

2. PM components that are economically advantageous compared to components made by machines, poured or forged. Structural parts, such as connections to be used in vehicle construction, connecting elements, cams and planetary mechanisms, are a few examples. The core of this type of production is iron-based components, but reasonably large quantities of products in copper, brass, bronze and aluminium, as well as more rarer metals like beryllium and titanium, are also made.

If, from a geometrical point of view, these technologies are not of primary interest for the precious metal industry, some of their less traditional variants can produce particular characteristics in the final product that would otherwise not be achievable and can therefore represent a substantial innovation in the fashion accessory field.

FAST technologies

Field Assisted Sintering Techniques can produce components with superior mechanical characteristics in a very short time. The principle at the basis of this series of technologies is the rapid supply of energy onto the powder given by an electro-magnetic field at relatively low frequencies (<500 Hz) [5]. It is the speed of the process that leads to enormous advantages, both from a productivity aspect and in terms of controlling the properties of the item produced.

A large number of variants, such as Spark Plasma Sintering, Electro Discharge Sintering and Capacitor Discharge Sintering, belong to this series of technologies and the physical phenomena behind this type of sintering are still being studied.

Some of the phenomena that occur during sintering are atomic diffusion, interaction between the thermal, electro-magnetic and mechanical forces, possibly amplified by the porosity of the components, as well as plastic phenomena favoured by the current flow through the conductive materials (EPE electro-plastic effect) [6].

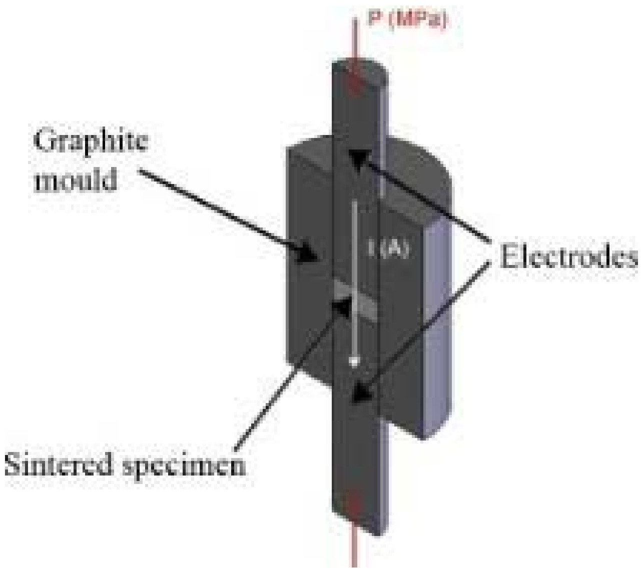

Figure 5 Diagram of a FAST device in which the electrodes also do the pressing.

One of the techniques in this series which has particular importance is EPS (Electron Power Sintering). Deriving directly from Capacitor Discharge Sintering, this technology achieves compacting at a density that comes very close to the theoretical compactness of a component with one single electro-magnetic impulse with a reduced duration (30-100 ms) while simultaneously applying axial pressure [7]. The high speed of this technology inhibits any crystallisation phenomena which are typical of thermal processes, thus obtaining extremely fine and nano-structured micro-structures with a much greater repeatability than the other technologies. The non-sustainability of the thermodynamic laws in this arc of time also makes it easy to obtain metastable compounds [8].

These innovative technologies offer the potential for numerous practical applications, primarily applications linked to producing items with theoretical density and with extremely interesting mechanical characteristics without the need of further, secondary plastic deformation or surface treatment operations. The use of 18K, nano-structured gold powders, for example, leads to achieving extremely hard compact solids (close to 300 HV) for applications that require optimal resistance to wear and tear and scratching, and give much greater results without having to perform secondary treatments.

INJECTION TECHNOLOGIES

MIM

"The gold industry finds itself in a privileged position for having adopted the MIM technology since the many advantages of this technology can be widely applied to sectors, such as gold, where the cost of the raw material is very high." Such wrote J. T. Strauss in 1996, inviting the jewellery sector to consider the undisputed advantages that applying MIM could bring [9].
The roots of MIM go back about 80 years when the first patents and the first articles on Ceramic Injection Moulding appeared [10]. Deriving from the injection moulding technology for plastic materials, Metal Injection Moulding (MIM) foresees the use of an injection press through which a plastic mass, made up of a blend of metal powders and polymeric binding materials, is allowed to flow into a metal mould (mono or multiple, simple or complex). Injection into the mould is guaranteed by the addition of the binding material given by the combination of various plastic components: polymers, waxes, additives. The blending of metal powders and binding materials is performed in hot mixers so as to obtain perfect homogeneity, and is then granulated [11].

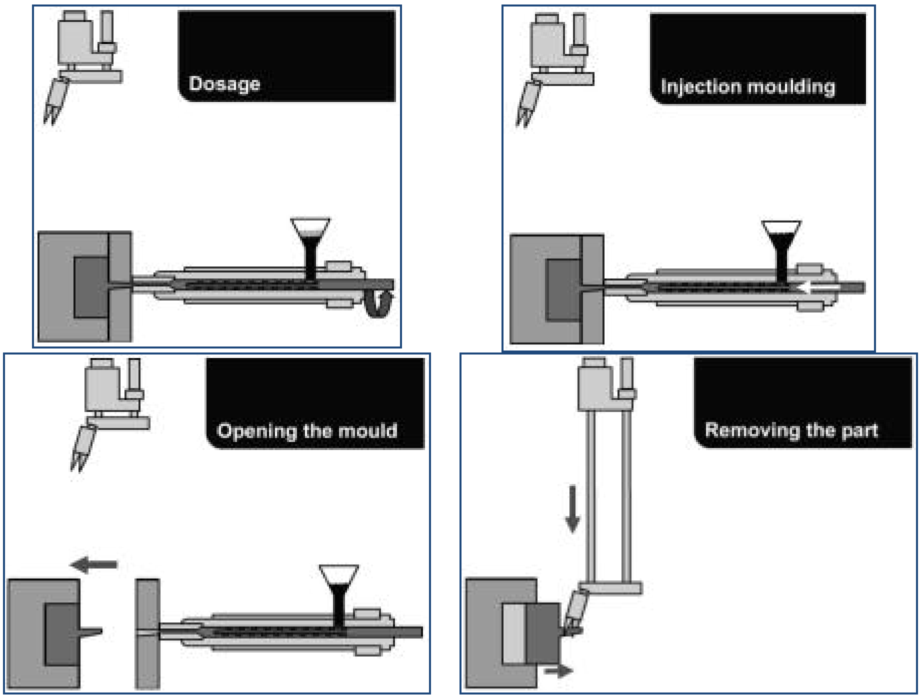

Figure 6 Diagram of the MIM injection process, the injection mixing stage, injection, mould opening and item extraction.

This feedstock, (generally made up of a 15-30% volume of binding material), manages to flow extremely well even inside complex cavities and gives the final product precise geometric characteristics in terms of surface finishing and geometric tolerances deriving from the metal mould into which it was injected. The solids extracted from the mould then undergo the process of eliminating the binding material (either thermally or chemically) and then go through a hot-sintering densification process. This process leads to the final densification of the metal compact and an isotropic and predictable

reduction in size. Sintering ovens are optimised for MIM processes. They are fitted out in such a way as to treat, by removing it, the part of the binding material which the pieces still contain and by having a sufficiently clean atmosphere at the sintering temperature.
Due to being able to produce small and geometrically complex items with a close to theoretical density and a good surface finish, MIM is in direct competition with traditional technologies in the gold sector, such as lost wax casting [12].
One of the applications that is surely of great interest is the production of watch cases. Many watch producers throughout the world are now using MIM to make cases and straps, including those made of precious metals, due to the tolerances obtained and the reduction in waste material (compared, for example, to shaving processes). The introduction of MIM has led to significant cost reductions compared to hot forging and mechanical processing. Furthermore, it has also led to a cheaper means of producing new shapes, which have modernised the watch industry.
Another sector strictly linked to jewellery and which uses MIM, is the spectacle industry. There are many examples of famous producers who use MIM to produce the components of their glasses, including those made of "difficult" materials like titanium. An interesting example is that of a particular spring joint used in the frames of Tag Heuer glasses in 316L. This component unites design with functionality. In fact, it provides excellent functionality combined with a soft movement of the two MIM pieces, integrated flexibility and a perfect surface finish that is absolutely necessary in the spectacle sector. Innovative design: a "clean" look - no holes, no borders, invisible screws on the frame and perfect integration with the frame design.

ADDITIVE MANUFACTURING TECHNOLOGIES

For several years now, additive manufacturing technologies have held considerable appeal in gold industry applications, both as instruments for traditional processing (the creation of prototypes or master models for rubbering) and as an integral part of the processing itself (direct resin casting). The main reason for this interest is linked to the possibility of creating geometrically complex items, which are often extremely fine or hollow, without having to spend longer over the traditional process steps.
Additive processes conducted on metal, and especially the technologies that belong to the rapid manufacturing group, are therefore of greater interest in a sector where the possibility of producing complex, unique and highly customisable items is of undisputed added value [13], [14].
Two PM technologies from those available are meeting with particular interest in the gold industry: Selective Laser Sintering and Selective Laser Melting.

SLS/SLM

The considerable interest in producing metal items from CAD designs, in contained times and without the need of intermediary steps, has been the driving force behind research and optimisation activities concerning powder bed technology, widely used in the aerospace and biomedical sectors, applied to the gold industry.
It involves a series of technologies, in their various constructive variants [15], that foresee creating a three-dimensional object from powder (in this case metal powder) by solidifying successive layers of material with the help of a laser. The processes are subdivided, in turn, into several categories, mainly in regard to the densification process used. Selective Laser Sintering (SLS) [16] refers to when the powders are not melted but are sinterised instead, and Selective Laser Melting (SLM) [17] is when the powder particles are melted next to each other to create a dense compact.

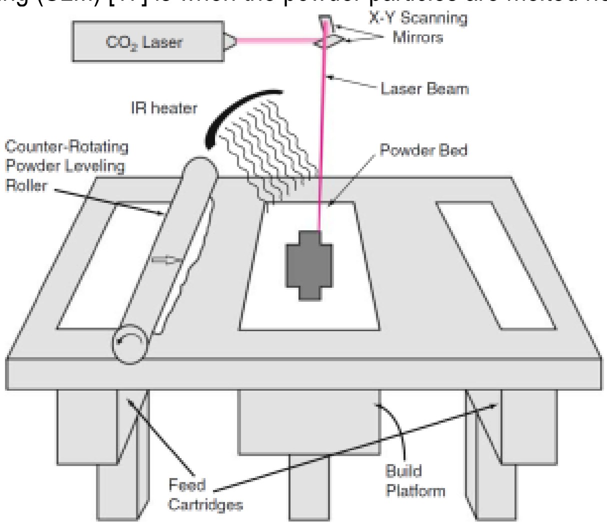

Figure 7 Diagram showing an example of powder bed laser technology

Both processes work by exploiting the creation of successive solid layers, solidified gradually by the action of a laser whose path is generated from a CAD design of the model being created. From many aspects, the two technologies are very similar and their optimisation is parallel (optimisation of the sizes and composition of the powders, generation of supports, re-use of any materials not treated thermally).

However, the two techniques do differ substantially from a metallurgic point of view since they involve different physical phenomena: phase and liquid flow transformations for the SLM process against scattering phenomena in the SLS process. If on the one hand, SLM, with the appropriate choice of granulometric distribution of the powder and process parameters, produces extremely high density, SLS can make components from compositions which would otherwise be very difficult to obtain or from hard metals to the detriment of density, which will then have to be optimised by a secondary thermal treatment.

Fcubic

At the same time as the powder bed process, considerable interest has also been aroused by a process called FCubic, which unites the creative simplicity of a 3D mould with the opportunities that sintering provides [18]. With this technology and a device similar to 3D moulds for prototyping in polymeric materials, metal powder components, kept together by a thin layer of polymer binder, can be produced. This three-dimensional compact (in its green state, and therefore with no mechanical properties), must then undergo a binding material elimination process and hot-sintering similar to what is required for the MIM process.

In this way complex geometric components can be produced without the need to generate supports for their construction and the hot-sintering phase ensures achieving high levels of density.

Figure 8 Example of geometrically complex fashion accessories produced using the FCubic technology

LIMITS

The possibility of the mass introduction of powder metallurgy technologies into the gold business cannot ignore considering a series of factors and the fundamental meeting of certain requirements that are typical of the sector, such as:

- Surface finish: this factor, which is critical to the sector, is favoured in those applications that include shaping in moulds, where the degree of surface finish significantly affects the final component. The study and development of innovative surface finishings, suitable for producing goods by powder metallurgy is, moreover, an undisputed advantage for promoting the use of all powder metallurgy processes.

- The final density of the compact: the process parameters are the main factor considered in evaluating powder metallurgy technologies as an alternative.

- Productivity and Flexibility: the possibility of producing items directly from CAD, without having to use moulds or punchers, leads to enormous production flexibility. On the other hand, for large lots, the possibility of relying on a mould with strict dimensional tolerances leads to production time and cost optimisation.

- Geometric complexity: this depends on the type of process and is one of the discriminating factors between the various processes.

- Mechanical properties and innovative characteristics: the chance to obtain optimal or incomparable hardness and resistance compared to traditional technologies is one of the strong points of powder metallurgy processes in general.

- Variety of producible alloys: this is still a limitation when compared to traditional micro-fusion but is bound to become less so as PM techniques become more widespread and selective.

- Investment in different equipment compared to that used in traditional gold processes.

CONCLUSIONS

Powder Metallurgy has proven to be a sufficiently versatile technology which, in its more or less innovative forms, can meet the different needs of an increasingly varied market, such as the gold sector. The application of Powder Metallurgy therefore opens a whole range of opportunities, both in the production of a high number of identical objects, because they can be produced rapidly without having to undergo further processing and with a minimisation of waste material (referring to Metal Injection Moulding technologies or Field Assisted Sintering Technologies where a metal mould is required), and in the production of very small lots or one-off items, including prototypes, such as with Additive Manufacturing technologies (FCubic and SLS/SMS).

The multi-faceted aspect of this series of technologies therefore arouses substantial interest to further develop powders and optimise the various process parameters, in order to evaluate the possibility of substituting the different traditional production processes with Powder Metallurgy technologies.

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