OPPORTUNITIES OF POWDER METALLURGICAL PROCESSING OF PALLADIUM AND PLATINUM JEWELLERY ALLOYS

Jochen Heinrich[1], Thomas Laag[1], Thierry Copponnex[2]

Affiliation:
[1] C. Hafner GmbH + Co. KG Precious Metals + Technology
Maybachstr. 4, 71299 Wimsheim, Germany
[2] Hilderbrand & Cie SA
Route de Jussy 29, 1226 Thônex, Switzerland

Introduction:

Alloys of Platinum Group Metals (PGM) show outstanding characteristics for jewellery and watch making: they are precious, strong and white. 50Pt50Rh is one of the most outstanding alloys for high-end jewellery with a hardness of up to 400 HV, tensile strength up to 1200 MPa and a yellowness index of 8. At the same time, these alloys represent the most challenging materials with respect to processing, refining and high costs in capital. Powder metallurgy (PM) of PGMs is an essentially different processing practice from conventional manufacturing. We would like to give an insight into the production of platinum and palladium powders and their processing by additive manufacturing (AM) respectively laser metal fusion (LMF). Topics to be discussed cover comparisons of popular and new alloys including their material properties with respect to colour, microstructure, mechanical properties and workability. Many indicators suggest that product manufacturing from platinum and palladium alloys by PM can help making production more efficient, environmentally friendly, and customer oriented. It is shown that the combination of PM technologies such as AM with CNC-machining and/or heat treatment is a complementary future state of the art for resource-efficient manufacturing of high-quality jewellery and watches as well as for technical or medical applications.

Conventional processing of PGM alloys:

Traditional processing of PGM alloys usually includes the production of semi-finished products, the manufacture of jewellery articles by punching and CNC-machining closing in a recycling loop of scrap if possible and the end-of-life refining.

The production of semi-finished products starts with alloying and casting of ingots or bars. Typically, vacuum induction melting (VIM) furnaces are used. These melting units are fundamentally different from the continuous casting machines used for gold and silver processing, which can process large amounts of metal at low cost. A VIM is a gas-tight, closed melting system with water-cooled walls and a powerful induction heating system used to reach the high melting temperatures of platinum. Protective inert gas and high-performance pumps to generate the vacuum in the melting chamber are required. Normally, the crucible consists of costly zirconia ceramic. Cost-effective graphite crucibles are not suited because platinum and palladium alloys react with carbon. The alloys become prone to reactions with oxygen and carbon precipitations influence the deformation behaviour during further forming processes.[1] The advantages of melting in a VIM furnace are the removal of dissolved gases, e.g., oxygen and hydrogen, with vacuum, and it is the safest way to melt what are considered large quantities of PGMs at such high temperatures (2000°C). However, the disadvantage is the great expense and effort to produce starting material (cast parts, ingots, bars, etc.) to manufacture sheets, wires, tubes or casting cubes of platinum or palladium alloys and the limited amount of metal per casting. It is a batch process and the melting quantity is limited. PGM cast parts normally have good workability when the deformation and annealing processes are controlled. But the resulting amount of scrap is often high from removing sections with shrinkage cavities, from surface machining to produce defined surface finishes and from drilling chips when producing tubes. This means that the material input factor is high and the amount of recycling is high. It is possible to use predominantly scrap for re-melting. There are risks to loss and contamination and as well as an increase in material stock level, therefore possible cost increases.

Then, manufacturing of jewellery follows one of two paths. On the one hand, jewellery is investment cast and then further processed. Investment casting is the opportunity to produce parts close to the final shape. This means that the quality of jewellery is determined by the quality of the castings. Investment casting is a challenging task in particular for casting of 950Pt, but it is individual and fast. Many studies have been carried out in the past to control the quality and to understand the occurrence of casting defects. Extensive works in the last years by Klotz et al.,[2] Frye et al.[3], and Maerz et al.[4] reported the effects, problems and opportunities for quality improvement of platinum casting through, for example, hot isostatic pressing (HIP), prevention of crucible reaction, special gate and sprue design or correct choice of alloy and investment powder. The bottom line is that casting platinum is more difficult than casting gold or silver. Contamination by the ceramic crucible during melting is a problem that the material will become brittle. Refining of residues is essential to ensure the quality. On the other hand, manufactured jewellery from semi-finished products like sheets, tubes or wires can be used for industrial jewellery manufacturing or for watch making. The material quality is primarily determined by the quality of the semi-finished product. PGM semi-finished products have been produced on an industrial scale and are quality tested. The material input factor is high. Scrap often consists of chips from CNC processing. Chips are normally end-of-life scrap and must be refined before reuse.

Finally, a certain part of PGM scrap is recycled in a closed-loop production process for reuse as internal scrap. The pre-condition is that the scrap is clean and dry without any foreign material or chemical contamination. Pure PGM scrap is fairly easy to recycle and turn into new products due to vacuum melting and casting again, provided a proper scrap-to-refined-metal ratio is used to ensure quality and to manage risks. End-of-life refining of PGM scrap, in contrast to recycled scrap, means a complex and time-consuming hydrometallurgical refining process. The standard way to recover platinum from platinum scrap, for example, starts with the dissolution of the material and, because platinum is a very noble precious metal, this is complicated. The solvent used for this is highly corrosive aqua regia, a mixture of nitric and hydrochloric acids to produce a leach solution containing Pt and other metals. The platinum from the specially treated leach solution is separated by precipitation. The Pt is precipitated as ammonium hexachloroplatinate $(NH_4)_2[PtCl_6]$ or potassium hexachloroplatinate K_2PtCl_6 from the solution. Dissolving and precipitating need to be repeated until the solution is pure enough. This platinum salt looks bright yellow when it reaches high purity. The reductive precipitation of platinum in a hydrochloric acid solution is carried out afterward. Then, the precipitate is calcined to produce Pt sponge, which is further treated to produce pure Pt metal by vacuum melting. In the platinum recovery process, chemical substances or mixtures are necessary but could be dangerous. This has resulted in high standards with respect to operational safety, waste gas and water treatment. This recycling process requires very special chemical facilities in an industrial area and a qualified staff. The company must use special due diligence and is subject to very high requirements of German and European legislation, as well as regulations by the Responsible Jewellery Council (RJC). The effort for managing the process and the regulations is considerable. Unfortunately, in many cases there is no other alternative other than refining; otherwise, the material quality and the exact content of platinum or palladium cannot be guaranteed.

In summary, the traditional processing and refining technology of PGMs is characterized by many production steps, the need for special machinery and tools, a high fresh material input factor, and a long and complex refining process. These make the traditional processing of PGM metals, especially platinum and palladium alloys expensive and material-intensive. Powder processing of PGMs opens a window of opportunity to make the process shorter, to improve the quality and to reduce the material input factor.

Selected PGM alloys with outstanding properties:

We have selected various alloys of our portfolio for the experimental work in this study. In the following, two major alloys are briefly described:

- 95PtAu: C.HAFNER developed a universal 950Pt alloy with high strength and extraordinary casting performance. It is a four-component alloy with 95 % platinum content and gold, indium and ruthenium as alloying elements to adjust the desired properties like a good hardness, a perfect white colour, a low melting range, a fine microstructure, the best biocompatibility and high ductility. Gas atomized powders are spherical, easy to handle and show a very good performance and a high reusability in AM.
- 50Pd50Rh is an alloy with a rhodium content of 50 %. The alloy is perfectly white like rhodium plated and of a high hardness of up to HV 350 achieved by hot rolling. 50Pd50Rh is difficult to process traditionally due to the high hardness and its high liquidus temperature of 1800° requiring powerful casting equipment. It is essential to execute the first deformation steps by hot forming or by forging. The working temperature for hot forming needs to be above the recrystallization temperature of about 1200 °C, i.e. special furnaces are necessary. A normal manufacturing process can be performed only after hot forming and the regeneration of the cast microstructure. Special melting, forging and annealing equipment are widely not available and make the manufacturing process expensive. On the other hand, powders of the alloy behave like any other Pt powder. These characteristics make 50Pd50Rh predestined for PM technologies like Metal Injection Moulding (MIM) and AM.

Significant quantifiable properties of the alloys are listed and compared to literature data of other common alloys in table 1. The data does not include soft skills like malleability, suitability for stone setting and the effort in polishing.

Table 1 Properties of selected PGM semi-finished products

	95PtAu	95PtCuGa	95PtRu	50Pd50Rh
Hardness [HV]	165-270	160-235	125-210	185-350
UTS [MPa]	500-1000	430	410-800	680
Yellowness Index [YI]	10	13	9	8

Production of PGM powders:

There are various techniques for producing metal powders according to their metallurgy, configuration and costs. As processing technologies like AM and MIM usually require powders of high sphericity, we focus on gas atomization of melts for production of precious metals powders. The gas atomizer with the most spherical powders, according to our experiences, uses the Nanoval-process.[5] This system is also capable of atomizing the whole range of precious metal alloys including high-melting PGM alloys with Ir and Rh. The process is based on a Laval-type nozzle placed concentric below a heated feeder of a melt stream at the opening of a pressure chamber (see Figure 1). The nozzle's converging cross section accelerates the inert atomization gas to the velocity of sound while the melt stream is compressed to a thin filament. The filament finally atomizes at the transition to the diverging cross section of the nozzle. This setup creates very fine droplets with very little convection to provoke the formation of powder particles with undesired satellites. While powder batches produced by free fall or coaxial (so-called close-coupled) nozzles have mean particle diameters [d50=d(Q3=50%)] of down to 30 µm to 70 µm, respectively,[6,7] the Nanoval process reduces that value to as small as 15 µm (Figures 2 and 3).

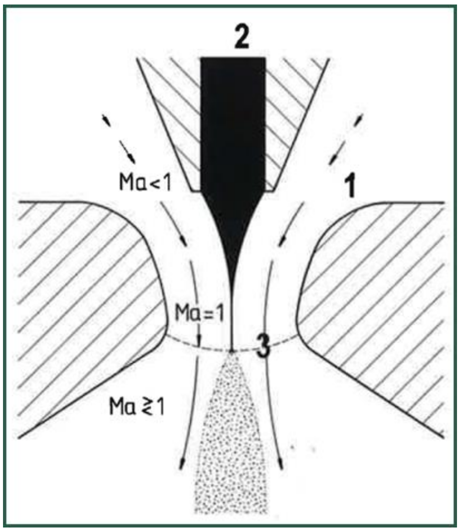

Figure 1 Laval-type nozzle within the Nanoval process[5]

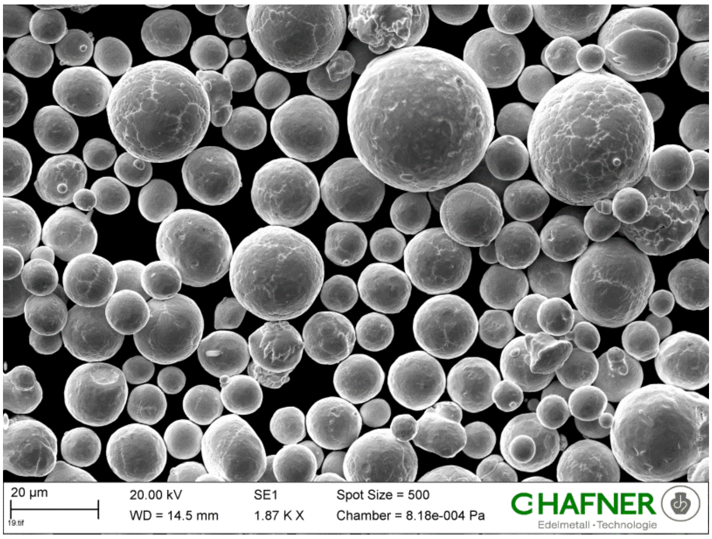

Figure 2 95PtAu powder particles at high resolution

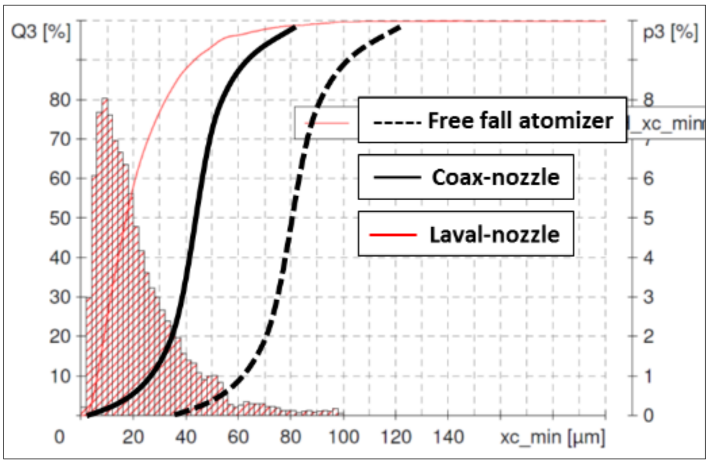

Figure 3 Typical particle size distributions for different atomizers

Classification

The small particle size of powders produced by atomization with the Nanoval process also correlates well with the desired particle size distribution (PSD) of powders required for use in AM and MIM resulting in a high yield. Figure 4 shows one of the PSDs of a 95PtAu alloy qualified for direct metal laser sintering (DMLS) manufacturing. According to experiences in material qualification for a DMLS process, a PSD with a range of 9 – 53 µm (lowest particle diameter $d_{1\%}$ = 9 µm to cumulative upper size limit $d_{99\%}$ = 53 µm) achieves the best combination with regard to density, surface roughness and feature size of AM parts made of 95PtAu. The yield for this PSD is up to 80% of an atomization batch.

The sizing process can be done by sieving or air classification. The limiting factor for selecting either method is not only the cut size, but the density of the powder and a reasonable classification rate must also be considered. Cuts containing small particle sizes are predestined for air classification because fine sieves are limited to a mesh size of ≥25 µm and very low throughput, i.e., low classification rates. On the other hand, cuts containing larger particle sizes are limited by the basic principle of drag, centrifugal forces and rotation speeds versus the density of the particles. Smaller cuts can be done by air classification while the large PSD cuts are executed by sieving.

The typical classification rate is 5-10 kg/h for air classification and up to 13 kg/h for sieving. Tumbler screening machines might have even higher rates although the focus of batch sizes and flexibility of system changes need to be taken into consideration.

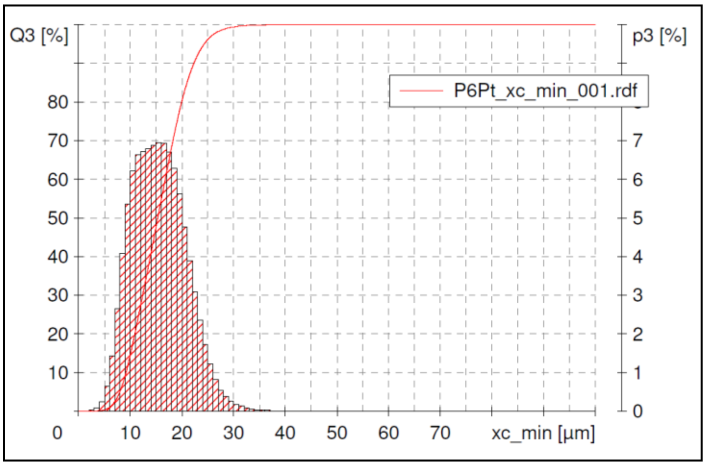

Figure 4 PSD of a 95PtAu *powder for AM*

Additive Manufacturing:

AM parts shown in this work were produced by Laser Metal Fusion (LMF), which is one of the numerous DMLS techniques based on a powder bed, a horizontal coating unit and a red laser source. The focus of process development and material qualification was the optimization of process parameters of hatch, contour and support strategies with regard to the specific metallurgy of the alloy, the PSD of the powder and the design of the part. Parameters included slice thickness, laser power, scanning speed, scanning order, hatch distance, field offset, border distance and platform material — in total, at least 14 more or less individual parameters. Although qualified parameter sets are intellectual property, it is important to point out some general crucial issues:

- Energy: Modern systems with several hundred watts of actual output provide enough energy for building a melt pool even for materials with a high liquidus temperature like Pt. However, the quality of the melt pool is influenced by material-specific reflectivity, absorption and thermal conductivity. For example, the reflectivity of a 1070 nm (red) laser wave by Pd and Pd is about 70% and more than 90% by Au, Ag and Cu. DMLS systems with a green laser source would reduce the reflectivity to about 70% for Au.[8]
- Ambient conditions: Unavoidable smoke during the process needs to be dragged away reliably without disturbing the energy input and contaminating the powder bed. Additionally, the partial pressure of oxygen needs to be limited to 0.1% for PGM powders to reduce porosity, according to recent studies. With this limit, powder was reusable many times without an oxygen enrichment exceeding 100 ppm. C. Pogliani et al. recommended a limit of 0.15% for 18K gold alloys.[9] Furthermore, DMLS systems for precious metal applications are usually small and not engineered to have temperature control of the powder bed like larger systems. The resulting temperature fluctuations can reduce the quality tremendously in terms of density and accuracy.
- Design: Although the LMF system can provide high-energy outputs, bulky or filigree designs have different limits in energy dissipation. While bulk sections can be built at high building rates, small features or thin-walled structures need a reduced energy input to avoid pores and deformations due to residual stresses. These issues can be

addressed by a design optimization for AM, different parameter sets with scanning strategies dedicated for certain features, and software that calculates risk depending on parameters such as heat gradients due to slice-by-slice scanned volume changes versus part orientation.

In addition to these parameters, the support structure also needs to be adapted to the design, considering requirements like support of overhanging surfaces, thermal conductivity and a steady connection to the substrate material. Various requirements can result in an impossible build job, e.g., a bulk section requiring strong, large-area supports at a position difficult to access for finishing, or easy-to-remove thin supports for a bulk part with insufficient heat dissipation and weak connection. In some cases, scanning pauses or a change of substrate material can help. According to our experiences, copper or bronze substrate plates are recommended for processing most precious metal powders. Finally, an optimization of the design might be necessary, too, or even inevitable.

Although marketing departments and technology scouts promise the impossible can become reality by AM, there are certainly limits of feasibility, size and accuracy. On top of that, quality standards of the jewellery and watch industries are very high. Final finishing with tools is mandatory to achieve flawless, perfectly shiny surfaces or to guarantee tolerances of down to 5 µm typical for the watch industry. The combination of AM with CNC machining not only facilitates the serial production of parts with high accuracy, it also allows manufacturing additively at high build rates without spending a large amount of time on contours and support structures. Figures 5 and 6 show examples of hybrid parts that were produced by LMF and CNC lathing. At the same time, the hybrid manufacturing method of CNC-machining of AM pre-products with a material allowance of only up to 0.5 mm reduces significantly the chipping volume, tool wear, time and refining efforts and in the end the total costs. Just imagine the difference in volumes when compared to punching grids or machining off solid semi-finished products!

Figure 5 PGM tensile specimens produced by LMF and CNC machining

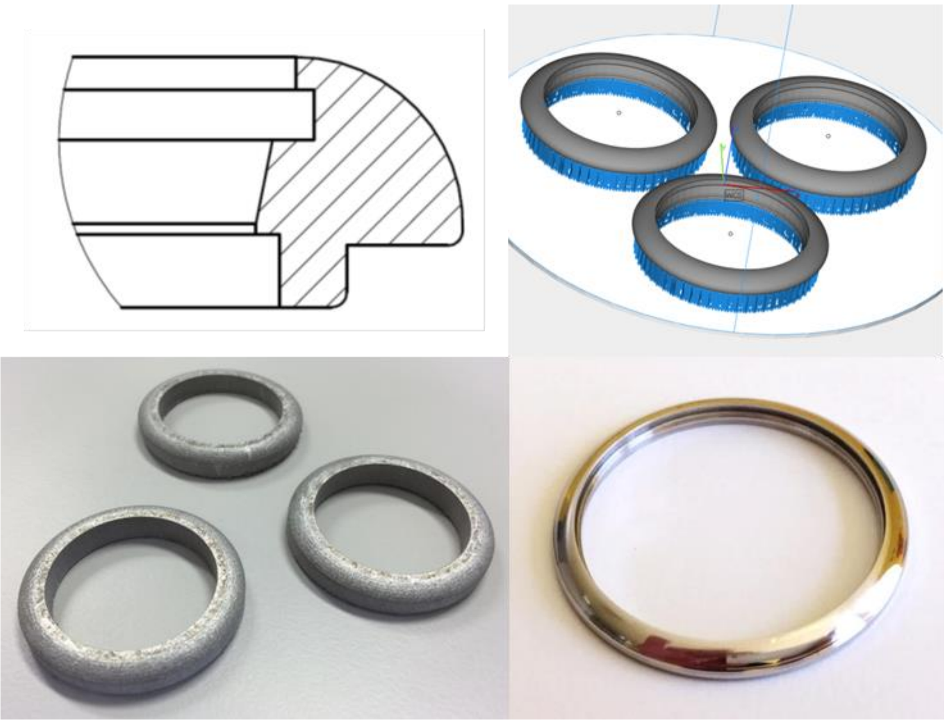

Figure 6 Watch bezels made of 95PtAu or 50Pd50Rh produced by LMF and CNC machining

Metal injection moulding (MIM) comes into play for the production of larger series. Costs for feedstock production, injection moulding machines and tools, and the heat treatment efforts need to be covered. Of course, it is beneficial to have similar designs of the same material that can be produced in one production line including the extra step of green body milling. The yield is unbeatable by traditional processing techniques as MIM produces complex parts in near-net-shape, and even sprues can be recycled immediately, resulting in a total of about 25% of end-of-life scrap that needs to be refined. The proof of concept with different PGM alloys was performed in earlier studies.[10]

Material properties and influences:

Requirements of the jewellery and watch making industries are probably the most challenging with regard to material defects and surface quality. Meeting or exceeding those is fundamental for acceptance of any processing technology. An entire compaction of the material is an inherent effort in powder metallurgical processes. Process parameters for each manufacturing step such as atomization of spherical powders, powder classification, feeding the process with powder, melting or sintering of powder particles and post-processing are subject of continuous optimization. In this study, the quality of powder metallurgical manufactured parts was evaluated by metallographic investigations and mechanical testing. Samples were built of various alloys including 95PtAu and 50Pd50Rh using the LMF technology.

Metallographic Data:
With the aim of a minimum material density of 99.9 %, numerous parameterization iterations were performed and cross sections in different orientations were prepared by established metallographic procedures including electro-chemical etching with sulfuric acid. The microstructures of AM materials typically follow a very ordered pattern due to the digital process. The grain size is usually significantly lower in comparison to traditional cast materials (exemplary photomicrographs in Figure 7). Grains for as built pieces of 50Pd50Rh

are about 50 µm small and can be as small as about 20 µm as seen for 95PtAu (table 1). However, grains can grow much larger in vertical direction with sizes up to several millimetres as seen in cross-sections of LMF parts which are built at disadvantageous high energy inputs (Figure 8). The columnar grain shape is promoted by high temperature gradients during the scanning process and high purities of the material, reminiscent of growing single crystals by zone melting. The resulting non-uniform microstructure can cause an anisotropic material behaviour.

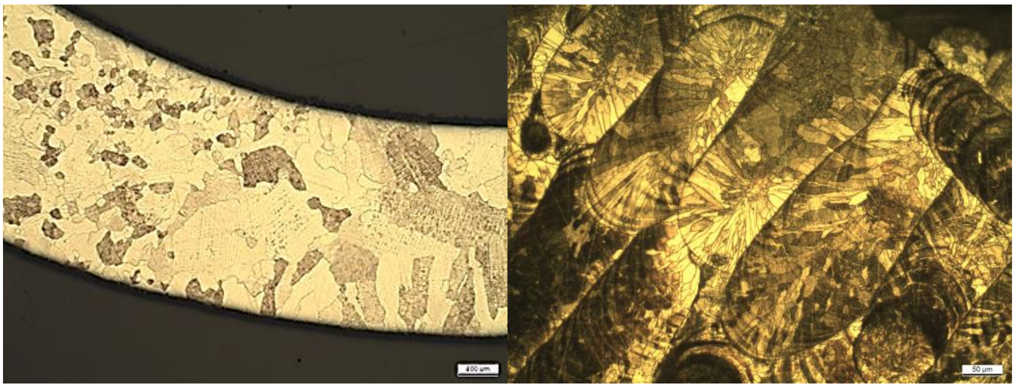

Figure 7 Microstructure of a casting and LMF sample

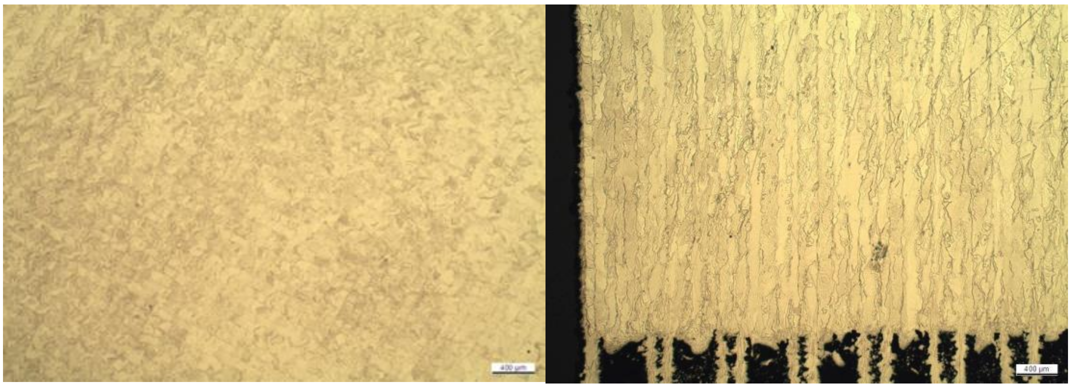

Figure 8 Microstructure of a LMF sample at high energy input (a: horizontal plane, b: vertical plane)

As defects like segregations and shrinkage cavities are typical for metallic structures, the micrographs were also used to determine the overall density of the specimen. The density was determined statistically by a set of ≥18 micrographs covering the entire surface and the use of the image analysis software imageJ®. The highest density achieved for LMF samples made of 95PtAu and 50Pd50Rh was 99.97% with a layer thickness of 20 µm and PSDs of 9-53 µm and 5-53 µm, respectively (table 2). These values can vary significantly with slight changes in the basic material like powder shape and classification as well as AM processing parameters like scanning strategy and heat treatments. Developing and monitoring those key parameters are unavoidable for the successful application of the technology and to fulfil the quality standards.

Mechanical Properties:
Mechanical testing was focused on the determination of hardness and tensile strength including correlations with post-processing steps. The hardness of semi-finished products of 95PtAu varies from HV 165 - 270 for as-cast and a 70 % work hardened state, respectively (table 1). The hardness of AM parts is about 10 % higher in comparison to castings due to the small grain size of the digital microstructure (table 2). Age hardening is not possible for 95PtAu. Semi-finished products of 50Pd50Rh show hardness values from HV 185 in the as-cast state, HV 250 for age hardened material and up to HV 350 after hot working with 80 % deformation (table 1). As-printed LMF parts of 50Pd50Rh have a hardness of HV 240. AM parts can also be age hardened as achieved by hot isostatic pressing (HIP) (table 2).

Tensile testing of specimen made of 95PtAu conventionally by casting and by PM processes revealed slight differences in the ultimate tensile strength (UTS = 500 vs. 578 MPa, see tables 1 and 2). A significant increase of up to 1000 MPa can be achieved by work hardening. The UTS for 50Pd50Rh was observed at 682 MPa. Both alloys showed no differences in UTS depending on the stress direction observed in tensile testing for specimen built horizontally vs. vertically, i.e. the material can be considered as isotropic as expected for uniform microstructures. In earlier studies, an anisotropic behaviour was observed in tensile testing of 80Pt20Ir, i.e. strength depending on the direction of the stress vector. While the UTS in horizontal orientation reached values equal to semi-finished products (UTS = 620–650 MPa), UTS values for stresses applied in a vertical direction showed about 15% lower values. It was obvious that this anisotropy was related to the columnar microstructure and the different number of grain boundaries activated in the stress planes.[10]

Heat treatment parameters can influence the above mentioned results significantly, especially HIP. HIP can increase the density up to 100% as seen in LMF parts made of various alloys (see table 2 and reference 10). Additional possible effects of heat treatment are the influence of age hardening and a changing microstructure. As an example, studies of 95PtAu showed a grain growth during HIP (see figure 9). The result is a highly uniform microstructure with globular grains with a mean grain size of about 70 µm. Ductility is increased considerably (see figure 10) and the workability of the material should further improve. Short treatments for densification do not necessarily cause a relevant reduction in hardness. On the other hand, long HIP runs can further coarsen the microstructure and specimen show significantly lower mechanical properties compared to as printed samples. It needs to be noted that the yield strength (YS) is reduced from about 75 % of UTS to about 50 % UTS and the hardness is reduced to about 80 %.

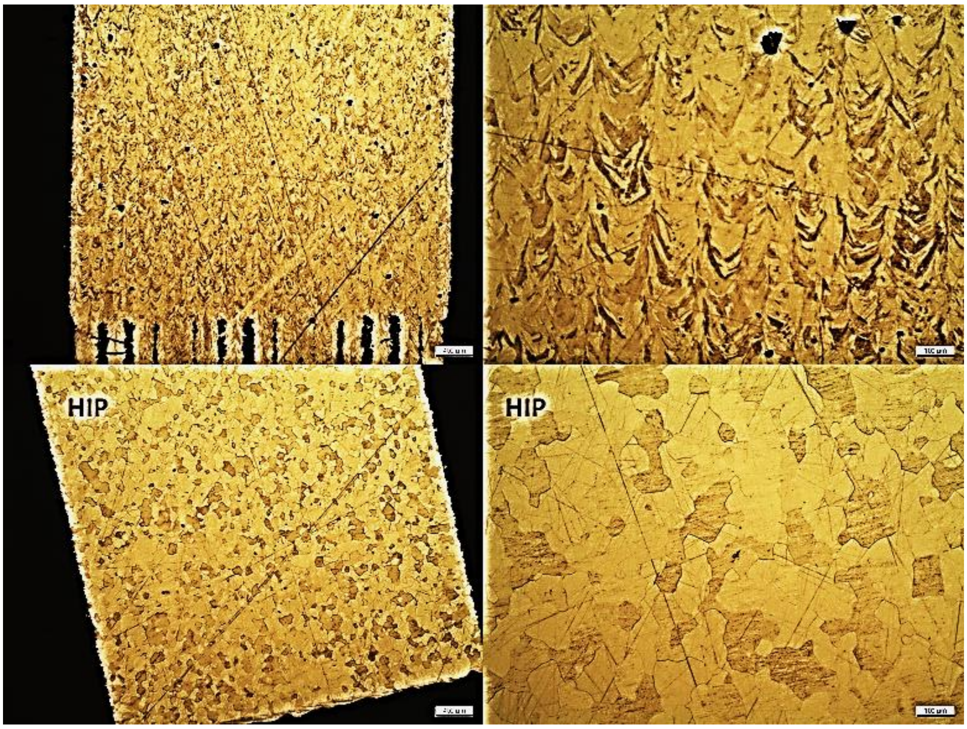

Figure 9 Vertical cross sections of a 95PtAu LMF sample at different magnifications without and with HIP-treatment

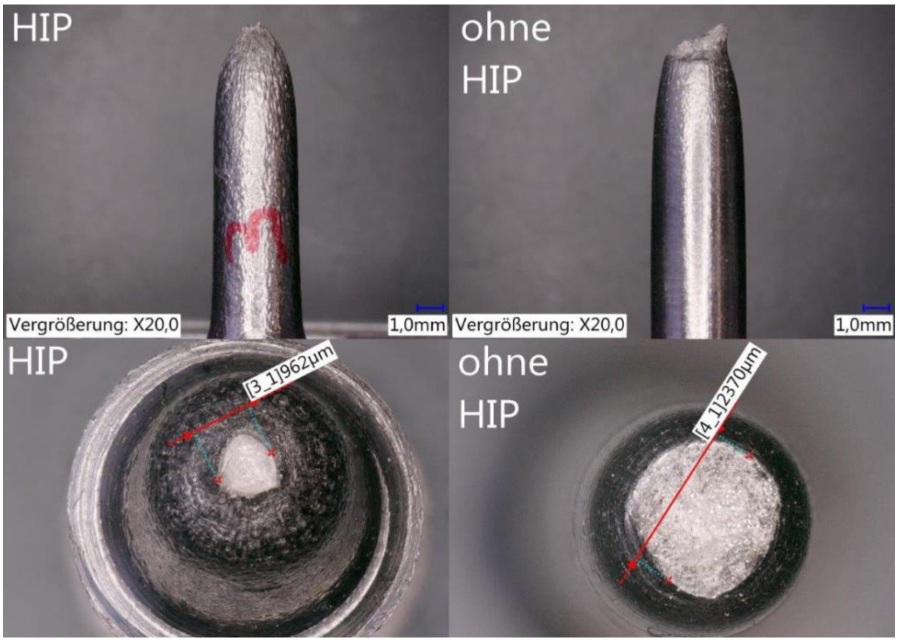

Figure 10 Fracture surfaces of 95PtAu tensile specimen with and without HIP treatment

Table 2 Properties of PGM parts

Method	LMF		LMF + HIP	
Material	95PtAu	50Pd50Rh	95PtAu	50Pd50Rh
Density [%]	99.97	99.95	100	100
Grain size [µm]	21	12	37 / 88	48
Hardness [HV]	186	240	180 / 151 short/long	258
UTS, z [MPa]	578	682	532	758
YS, z [MPa]	443	588	300	561

Conclusion and Summary:

Obviously, powders of various PGM alloys fulfilling the processing requirements of powder metallurgical manufacturing methods are available. This opens the opportunity to use PM methods for a less expensive and less material-intensive manufacturing of PGMs in comparison to traditional processing.

LMF as one of the DMLS techniques qualifies for the serial production of precious metal applications. Inherent for AM, LMF is recommended for the production of pilot series, small series and intricate designs. The combination of AM with CNC machining is a powerful hybrid manufacturing processing chain for the serial production of parts with high accuracy. MIM can be a supplementary processing method predestined for larger series. Prices scale rather little for AM in comparison to MIM where equipment and mould costs are considerably higher becoming economical at much larger numbers of pieces.

Comprehensive tests of PM parts by LMF were carried out to determine optimal process parameters to achieve a high density. Densities of LMF parts of 95PtAu and 50Pd50Rh achieve values of up to 99.97 %. The remaining porosity of 0.03 % is comparable to densities of cast products. Polishing trials were flawless suggesting that the residual porosity is neglectable. LMF parts reach even 100 % density by additional HIP treatments eliminating any defects and risks for the extremely high requirements of jewellery customers with regard to surface appearance. The LMF process causes a digital microstructure with extraordinary fine grains with sizes down to 20 µm. This value is impossible for cast products. The homogeneous microstructure is ideal for polishing and machining and properties can be tailored to a certain extend. Mechanical properties of PM parts typically slightly exceed the properties of castings. Additional age hardening to strengthen the material is possible. It needs to be emphasized however, that slight changes of processing parameters can have a significant influence on the part quality. Highest qualities are only achievable for the optimized system consisting of powder, equipment and process.

Yield, being a crucial key factor for the economic success of each process, is an advantage of PM over traditional processing of PGM alloys. The yield in exemplary business cases of watch parts was at approximately 10-20 % for traditional casting, rolling, punching and machining, at about 50-60 % for LMF and up to 75 % for MIM. The material input is about five times higher for the traditional vs. the AM route, i.e. factor five in cost in capital. The material allowance of punched parts is about three times higher than AM pre-products resulting in twice the chipping volume in subtractive CNC-finishing. The end-of-life refining scrap volume of all processing steps totals in a factor five for conventional vs. PM processing in combination with CNC-finishing. Of course, geometry and number of pieces have a strong influence on those calculations. In any case, the capital employed and refining efforts are directly related to the yield. For PGMs - being an expensive material group and costly to refine - it is highly recommended to use PM processes as long as sizes and geometries of parts are suitable!

Acknowledgements:

The authors would like to thank the organizing committee of the 2019 The Goldsmiths' Company Jewellery Materials Congress for their consideration of this contribution. We would also like to acknowledge the support in LMF technology of the companies Trumpf GmbH and Sisma S.p.A..

References:

1. G. L. Selman et al., “Carbon in Platinum and Palladium“ Platinum Metals Rev., 1970, 14-20
2. U.E. Klotz et al., “Platinum Investment Casting: Material Properties, Casting Simulation and Optimum Process Parameters,” The Santa Fe Symposium on Jewelry Manufacturing Technology 2015, ed. Eddie Bell et al. (Albuquerque: Met-Chem Research, 2015).
3. T. Fryé et al., “The Effects of Hot Isostatic Pressing of Platinum Alloy Castings on Mechanical Properties and Microstructures,” The Santa Fe Symposium on Jewelry Manufacturing Technology 2014, ed. Eddie Bell and J. Haldeman (Albuquerque: Met-Chem Research, 2014).
4. J.J. Maerz and T. Laag, “Platinum Alloys, Features and Benefits: Comparing Six Platinum Alloys,” The Santa Fe Symposium on Jewelry Manufacturing Technology 2016, ed. Eddie Bell et al. (Albuquerque: Met-Chem Research, 2016).
5. Patent DE 10 340 606 B4, "Vorrichtung zum Verdüsen eines Schmelzstrahls und Verfahren zum Verdüsen von hochschmelzenden Metallen und Keramikschmelzen,“ Nanoval GmbH, Germany.
6. Patent DE 4102101 C2, "Einrichtung zum Herstellen von Pulvern aus Metallen,“ ALD Vacuum Technologies AG, Germany.
7. Patent DE 10044364 C1, "Zerstäubungsaggregat zum Zerstäuben von Schmelzen,“ ALD Vacuum Technologies AG, Germany.
8. Günter Beck et al., *Edelmetall-Taschenbuch*, 2nd ed. (Heidelberg: Hüthig-Verlag, 1995): 172.
9. Christina Pogliani and Alberto Albertin, "Case Study of Problems and Their Solutions for Making Quality Jewelry Using Selective Laser Melting (SLM) Technology," *The Santa Fe Symposium on Jewelry Manufacturing Technology 2016*, ed. E. Bell et al. (Albuquerque: Met-Chem Research, 2016).

10. T. Laag and J. Heinrich, „Advantages and Challenges of Platinum Group Metals Powder Processing" *The Santa Fe Symposium on Jewelry Manufacturing Technology 2018* ed. Eddie Bell et al. (Albuquerque: Met-Chem Research, 2018).