## INVESTMENT CASTING OF PLATINUM GROUP METALS: CASTING CHALLENGES, PROCESS PARAMETERS AND RESULTING MATERIAL PROPERTIES

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### 1 Abstract

Platinum group metals such as platinum and palladium alloys are challenging in investment casting due to their high melting temperature and reactivity. This paper reviews the work that has been done in recent years to better understand the challenges of the process. This included detailed characterization of the crucible and investment reactions, studying the role of the different process parameters, new alloy developments and the determination of microstructure and mechanical properties of the alloys on the market. The producers of crucibles, investment powder and casting machines were involved in the process optimization together with alloy producers and casters. The experimental work was supported by state-of-the-art simulation techniques of the alloy thermodynamics and the actual casting process (form filling and solidification). Post processing after casting, such as hot isostatic pressing (HIP), is becoming more common in jewellery industry due to the beneficial effect on the mechanical properties. So far, the focus was on 950 platinum alloys. The studies showed significant differences among the alloys in terms of castability and properties. With the information now available on process and properties, platinum casting is much better understood and reliable casting quality is achievable.

### 2 Introduction

Investment casting is one of the oldest production techniques for metallic materials. Especially for precious metals it has been used for several thousands of years. Most technical alloys, such as aluminium, steel, Ni-base or Cu-base alloys can be produced by investment casting. The process requires a series of steps as shown in Figure 1. In jewellery technology investment casting is the most established process for silver, gold, platinum and palladium alloys [1]. The effectiveness of investment casting depends on the properties of the alloys. Silver and gold can be cast quite easily with reproducible results and great detail of cast parts [2-5]. The process and possible defects are very well established [6-8]. The process of form filling and solidification can be simulated by computational fluid dynamics, which provides an opportunity for better understanding of the role of the process parameters and their optimisation [9-11].

The investment casting of platinum group metals (platinum and palladium) is more demanding than silver or gold due to their specific properties. Some studies of the jewellery investment casting process using platinum [12-15] and palladium alloys [16-21] have been conducted. Extensive literature sources about platinum investment casting can be found in

[15,22]. The material parameters of some precious metal alloys that are relevant to investment casting are reviewed in [14,23-25]. Numerous data are available for gold and silver alloys in reference handbooks [26,27]. Data for platinum and palladium alloys are scarce. Some basic data, such as the volume shrinkage during solidification have just recently been determined for 950Pt alloys [28]. Such data allowed the simulation of the casting process also for platinum alloys [22]. Mechanical properties and microstructure of platinum casting are now available for many commercial alloys [29,30].



d) <sup>2</sup> 13 14 15 16 17 18 19 20 21 Figure 1: Principle steps of the investment casting process

Preparation of wax models by wax injection into rubber mould or by 3D printing of wax/resin parts from 3D CAD data

Assembly of a wax tree. Different types are possible depending on the casting process and material to be cast.

Investing of the wax tree in a gypsum or phosphate bonded  $SiO_2$ -based ceramic.

Burnout of the flask overnight:

- Melting of wax
- Dehydration of gypsum/ phosphate binder
- Sintering of SiO2

Casting process by:

- Gravity pouring
- Tilt casting
- Centrifugal casting

into the pre-heated flask. Typical flask temperatures are 500-900°C, depending on alloy and part dimensions and shape

Devesting by water quenching. Water blasting and/or glass-bead blasting to remove investment residues. The image shows a typical platinum tree for centrifugal casting immediately after water quenching.

Cutting the parts off the tree, grinding, polishing and finishing of the parts.

Platinum alloys can be categorised into three different groups of soft alloys (< 120HV1), medium-hard (120-150HV1) and hard alloys (>150HV1). Soft alloys typically contain Ir, Cu, Pd+Co or Rh as alloying additions. Medium-hard alloys are obtained by alloying with Ru, and 950PtCo is just at the threshold from soft to medium-hard. Hard alloys require the addition of Ga or In, which are among the most effective hardeners of platinum [31].

# **3** Optimum process parameters for the investment casting of platinum and palladium alloys

Like any other production process, investment casting is prone to certain defects on the parts. Such defects can be separated into several classes [32,33]. The most important defects are poor form filling, investment reactions and porosity. Many parameters influence the final casting result (Figure 2). This makes difficult to identify specific parameters that are responsible for a certain defect. This paper describes the influence of process parameters on casting quality in case of 950Pt alloys. The control of many casting machine related process parameters is provided by computerized casting as shown in Figure 3 and Figure 4. Additional process control was achieved by measuring the melt temperature using a thermal imaging camera (Figure 3) and by mounting thermocouples inside the flask (Figure 4). Such temperature measurement was the basis for the computer simulation of the casting process.



Figure 2: The optimum casting quality is affected by process parameters, materials properties and post treatment processes.



**Figure 3:** The tilt casting process. Left: tilt casting machine (Indutherm VTC100V Ti) with thermal imaging camera. Centre: the pouring process. Right: time-temperature profile of the melting cycle

In tilt casting a conventional tree type was used as shown in Figure 1a). The parts were mounted on the main sprue in several layers with an angle of 45°. The particular machine used in this study has two separated chambers (melting chamber and flask chamber) which allow the use of differential pressure in both chambers in order to assist form filling. Both chambers of the machine were evacuated prior to melting. For the actual melting process the melting chamber was back-filled with argon in order to prevent oxidation or excessive reaction of alloy and crucible material. The flask chamber remained evacuated throughout the complete process. After melting and superheating of the melt by about 100 K the pouring process was started. Once the tilting process was completed the gas pressure in the melting chamber was immediately increased to 1 bar, which resulted in a pressure difference of about 1.5-2 bars between melting and flask chamber. Such pressure resulted in significant improvement of form filling. However, the melt has to be liquid inside the flask for the differential pressure to be effective. This requires a higher flask temperature compared to centrifugal casting.



**Figure 4:** The centrifugal casting process. Left: centrifugal casting machine, model TOPCAST TCE10. Right bottom: the centrifugal casting process. Right top: temperature measurement inside the flask.

In centrifugal casting the centrifugal force, the inertia of the material and gravity are three factors that control metal flow. Inertia only acts during acceleration of the spinning arm. The parts have to be mounted on the tree by taking into account the acting forces. Figure 5 shows two situations illustrating the role of inertia (red arrow) and centrifugal force (orange arrow). The green arrow stands for the resulting force. In our tests form filling and even solidification was completed during the acceleration of the spinning arm. Therefore, the parts have to be mounted at the right position. The trailing side promoted quick form filling of all parts at the same time. However, the melt tended to splash into the parts, which might result in cold shuts. The mounting of the parts on the leading side relative to the spinning direction provided the better solution. The melt is forced to flow along the main sprue to the tip of the tree from where the parts were back-filled part by part. The diameter of the main sprue was found to be important for the filling speed. A reduction of the main sprue diameter from 10 mm to 5 mm resulted in a significant reduction of filling time in both centrifugal casting and tilt casting. This was an important result in terms of casting quality and cost effectiveness.



**Figure 5:** Results of casting simulation show the influence of tree setup on form filling in centrifugal casting. Left: parts mounted on the trailing side. Right: parts mounted on the leading side of the tree

Melt temperature played an important role in form filling, but also in shrinkage porosity. Figure 6 shows the simulated porosity of a typical ring for two melt temperatures. In case of the lower melt temperature the porosity was higher in the complete ring section, especially in the sprues. Shrinkage pores at the connection of sprue and part will show up after sprue cutting and will require repair or even result in discarding the part. Sufficient superheating of the melt is therefore mandatory. We found that a superheating of the melt above its liquidus temperature of at least 100 K was required for 950PtRu, while 950PtCo required only 50-80 K to ensure complete form filling.



**Figure 6:** Results of casting simulation of 950PtRu: effect of melt temperature on porosity at a flask temperature of 850°C. Left: melt temperature 1850°C, Right: 1980°C.

Increasing the melt temperature can be detrimental to crucible and investment material. Both refractories are based on  $SiO_2$  ceramic, which forms several phases of different thermal stability.  $SiO_2$  shows excellent thermos shock resistance, which is important to enable the very high heating rates without crucible failure. However tridimyte melts at 1670°C, which is

below the liquidus temperature of most 950Pt alloys. Excessive heating (both duration or temperature) can result in softening of the crucible and dissolution of silicon in the alloy, which might then result in hot cracking and embrittlement of the alloy. This is especially the case for the alloy with high melting temperature such as 950PtRu. Therefore, melting duration and superheating has to be limited as far as possible. Crucibles with the addition of zirconia were found to show the best compromise of chemical stability and thermo-shock resistance.

The flask was pre-heated prior to casting to a temperature of 500-900°C. In most cases 850°C was used. Higher flask temperature promoted form filling, especially for filigree parts. However, the investment material has to withstand the hot melt, whose temperature is higher than the melting temperature of the refractory material. Local heating of the flask was simulated depending on melt temperature as shown in Figure 7. The sprues and thicker sections obviously showed higher temperature. Sharp edges or undercuts are critical regions where high temperatures occurred, which are close to or even exceeding the melting temperature of the refractory material. This resulted in rough metal surface with a glassy layer of molten investment and sub-surface gas porosity. Investment powders based on pure hexagonal  $\alpha$ -quartz showed higher stability compared to the ones that use different SiO<sub>2</sub> modifications such as  $\alpha$ -quartz plus  $\beta$ -christobalite and tridymite. Such highly stable investment powders are mandatory for high melting platinum alloys (e.g. 950PtRu). Lower melting alloys (950PtCo, 950PtRuGa) can be used with less stable investment powders.



**Figure 7:** Results of casting simulation: effect of melt temperature on investment reactions at a flask temperature of 850°C. Left: melt temperature 1850°C, Right: 1980°C.

Form filling is a critical issue for filigree items. We used a grid type sample in order to assess the form filling depending on casting machine and alloy. Generally speaking, centrifugal casting shows superior form filling ability as a result of the higher forces and higher filling speed. To achieve similar form filling of the same part by tilt casting required an increase of flask temperature by about 100 K. This is feasible with low melting alloys, but often exceeds the limits of investment stability in case of the higher melting alloys. The effect of alloy composition is shown in Figure 8. 950PtRu has significantly lower form filling compared to 950PtCo. The reason for that was not only the difference in melting temperature, but also the different segregation behaviour, as explained in detail in [22]. If small amounts of Ru were replaced by Co the segregation direction changes, which resulted in significant improvement of form filling. In the case of centrifugal casting only 0.7% Ru was effective to increase the form filling from about 20% to 80%. In the case of tilt casting about 2% Co were required to achieve the same improvement.



Figure 8: The effect of alloy composition on form filling in centrifugal casting and tilt casting.

Small changes in alloy composition were also found to reduce porosity. Shrinkage porosity is a general issue in casting that is caused by the volume reduction during melting. Major shrinkage holes have to be avoided by proper sprueing of the parts in order to achieve a directional solidification from the tip of the part towards the main sprue. Casting simulation can be effective in the optimisation of the sprue position and sprue dimension. Next to such macro shrinkage a second type of shrinkage porosity might occur with much smaller pore size. This co-called micro shrinkage is caused by interdendritic porosity that forms in some alloys, especially in 950PtRu. Micro shrinkage is controlled by segregation during solidification as described in [22]. If the segregation behaviour was changed by small addition of Co the micro shrinkage porosity completely disappeared (Figure 9). At the same time the small grain size of 950PtRu was maintained in contrast to the coarse grained alloy 950PtCo.



**Figure 9:** The effect of alloy composition on microstructure and porosity in centrifugal casting experiments (melt temperature 1885°C, flask temperature 850°C). As-cast condition. Left: 950PtRu5, Center: 95 PtRu3.5Co1.5, Right: 950PtCo5.

The finely dispersed micro shrinkage pores (Figure 10) in the as-cast condition reduce ductility [31]. They could be completely removed by hot isostatic pressing (HIP) [34]. This

increased ductility while maintaining the strength (Figure 11). A detailed description of the HIP process and its effect of mechanical properties and microstructure of numerous platinum alloys is given in [31,34].



Figure 10: Effect of hot isostatic pressing on the microstructure of 950PtRu5. Left: micro shrinkage pores in the as-cast condition, Right: porosity free microstructure after HIP.



Figure 11: Effect of hot isostatic pressing on the mechanical properties of 950PtRu5. Left: as-cast, Right: HIP.

### 4 Summary and conclusions

Platinum alloys can be categorised into three different groups of soft (< 120HV1), mediumhard (120-150HV1) and hard alloys (>150HV1). Soft alloys typically contain Ir, Cu, Pd+Co or Rh as alloying additions. Medium-hard alloys are obtained by alloying with Ru, and 950PtCo is just at the threshold from soft to medium-hard. Hard alloys require the addition of Ga or In, which are among the most effective hardeners of platinum [31].

Successful investment casting of platinum alloys requires careful selection of materials and process parameters. SiO2-based crucibles with addition of zirconia showed a good compromise of thermo-shock resistance and durability. Investment powders based on hexagonal  $\alpha$ -quartz showed superior stability and appear mandatory for high melting alloys to prevent investment breakdown and reactions.

Important and helpful indications about the tree design, positioning or inclination of the parts on the tree and the temperature distribution of the investment could be concluded from the casting simulation. Particularly in the case of centrifugal casting, where the acting forces are more complex, the casting simulation helps understanding casting defects and finding suitable solutions.

950PtCo has a good form filling compared to 950PtRu independently of flask and casting temperature. Form filling was better in centrifugal casting compared to tilt casting, because the acting forces are higher. Hence, in centrifugal casting the filling was faster and the melt temperature remained higher during filling. As a consequence, lower superheating was needed in centrifugal casting to obtain the same filling.

HIP largely eliminates internal micro shrinkage pores and thereby restores the ductility of platinum alloys to their full potential. This is reflected by a significant increase in ductility and especially reduction of area. The effectiveness of HIPing on ductility depends on the level of micro porosity.

The partial replacement of Ru in 950PtRu by Co significantly reduces shrinkage porosity while maintaining the small grain size that is beneficial for 950PtRu. It further improves the form filling significantly. The properties of 950PtRuCo alloys in the as cast condition hardly differ from those in the HIP condition.

### **5** References

1. Faccenda V, Ott D (2003) Handbook on investment casting. World Gold Council, International Technology, London, UK,

2. Fischer-Bühner J (2006) Improvement of Sterling silver investment casting. Paper presented at the JTF - Jewellery Technology Forum, Vicenza, Italy,

3. Fischer-Bühner J Computer simulation of jewelry investment casting. In: Bell E (ed) The Santa Fe Symposium on Jewelry Manufacturing Technology, Albuquerque, NM, USA, 2006. ISBN, pp 193-216

4. Fischer-Bühner J, Bertoncello R Silver casting revisted: the alloy perspective. In: Bell E (ed) The Santa Fe Symposium, Albuquerque, NM, USA, 2010. Met-Chem Research, ISBN, pp 227-242

5. Ott D, Raub CJ (1992) Gold casting alloy 14 and carat. Gold Technology 7:2-7

6. Ott D, Raub CJ (1992) Casting-gas pressure effects. Gold Technology 7:10-17

7. Ott D, Raub CJ (1992) Casting-surface properties. Gold Technology 7:28-31

8. Ott D, Raub CJ, Rapson WS (1992) Casting-porosity causes and prevention. Gold Technology 7:18-27

9. Fischer-Bühner J (2006) Computer simulation of jewellery investment casting. Paper presented at the JTF - Jewellery Technology Forum, Vicenza, Italy,

10. Actis-Grande M, Porta L, Tiberto D (2007) Computer simulation of the investment casting proess: widening of the filling step. Paper presented at the The Santa Fe Symposium on Jewelry Manufacturing Technology, Albuquerque, NM, USA,

11. Fischer-Bühner J (2007) Advances in the prevention of investment casting defects assisted by computer simulation. Paper presented at the The Santa Fe Symposium on Jewelry Manufacturing Technology, Albuquerque, NM, USA,

12. Trosch T, Lalire F, Pommier S, Völkl R, Glatzel U (2018) Optimisation of a Jewellery Platinum Alloy for Precision Casting: Evaluation of Mechanical, Microstructural and Optical Properties. Johnson Matthey Technology Review 62 (4):364-382

13. Fryé T, J. F-B Platinum alloys in the 21st century: a comparative study. In: Bell E (ed) The Santa Fe Symposium on Jewelry Manufacturing Technology, Albuquerque, NM, USA, 2011. Met-Chem Research, ISBN, pp 201-230

14. Klotz UE, Drago T (2011) The role of process parameters in platinum casting. Platinum Metals Review 55 (1):20-27. doi:10.1595/147106711x540373

15. Heiss T, Klotz UE, Tiberto D (2015) Platinum investment casting, part i: Simulation and experimental study of the casting process. Johnson Matthey Technology Review 59 (2):95-108

16. Klotz UE, Held FJ (2019) Development of new 950Pd investment casting alloys with superior properties. Paper presented at the Jewelry Technology Forum (JTF), Vicenza, Italy,

17. Mann MB Palladium: manufacturing basics for servicing, assembly and finishing. In: The Santa Fe Symposium, Albuquerque, USA, 2007. ISBN,

18. Battaini P The working properties for jewelry fabrication using new hard 950 palladium alloys. In: The Santa Fe Symposium, Albuquerque, USA, 2006. ISBN,

19. Fryé T Palladium casting: an overview of essential considerations. In: The Santa Fe Sympoisum, Albuquerque, USA, 2006. ISBN,

20. Battaini P Investment casting behavior of palladium-based alloys. In: The Santa Fe Sympoisum, Albuquerque, USA, 2008. ISBN,

21. Fischer-Bühner J, Basso A, Poliero M Challenges for Palladium Casting Alloys. In: The Santa Fe Symposium, Albuquerque, USA, 2009. ISBN, pp 129-150

22. Klotz UE, Heiss T, Tiberto D (2015) Platinum investment casting, part II: Alloy optimisation by thermodynamic simulation and experimental verifi cation. Johnson Matthey Technology Review 59 (2):129-138

23. Raykhtsaum G (2013) Platinum alloys: A selective review of the available literature. Platinum Metals Review 57 (3):202-213. doi:10.1595/147106713x668596

24. Wright JC (2002) Jewellery-related properties of platinum. Platinum Metals Review 46 (2):66-72

25. Battaini P (2011) Microstructure analysis of selected platinum alloys. Platinum Metals Review 55 (2):74-83. doi:10.1595/147106711x554008

26. Beck G (1995) Edelmetall-Taschenbuch. 2nd edition edn. Degussa AG, Frankfurt und Hüthig GmbH, Heidelberg,

27. Grehl M, Lox E, Sehrt U, Weis M (2012) Precious Materials Handbook. Umicore AG Co. KG, Hanau, Wolfgang, Germany

28. Klotz UE, Plevachuk Y (2016) Thermophysical properties of platinum-rich alloys measured by sessile drop experiments. High Temperatures - High Pressures 45:3-20

29. Fryé T, Strauss JT, Fischer-Bühner J, Klotz UE The Effects of Hot Isostatic Pressing of Platinum Alloy Castings on Mechanical Properties and Microstructures. In: Bell E (ed) The 28th Santa Fe Symposium on Jewelry Technology, Albuquerque, USA, 2014. ISBN,

30. Fryé T, Klotz UE Mechanical properties and wear resistance of platinum jewelry casting alloys: a comparative study. In: Bell E, Haldeman J, Carr M (eds) The Santa Fe Symposium on jewerly manufacturing technology, Albuquerque, NM, USA, 2018. Met-Chem Research, ISBN, pp 235-273

31. Klotz UE, Fryé T (2019) Mechanical properties of platinum jewellery casting alloys. Johnson Matthey Technology Review 63 (2):89-99

32. Fischer-Bühner J (2006) Defect Catalogue Silver Jewellery Investment Casting. FEM Forschungsinstitut Edelmetalle & Metallchemie, Schwäbisch Gmünd, Germany

33. Ott D (1997) Handbook on casting and other defects in gold jewellery manufacture. World Gold Council, Industrial Division, London, UK,

34. Fryé T, Strauss JT, Fischer-Bühner J, Klotz UE (2015) The effects of hot isostatic pressing of platinum alloy castings on mechanical properties and microstructure. Johnson Matthey Technology Review 59 (3):207-217

# 6 Brief speaker's biography



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