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Platinum Investment Casting, Part II: Alloy Optimisation by Thermodynamic Simulation and Experimental Verification

Improved casting results found with addition of cobalt to platinum-ruthenium alloys

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Two widely used jewellery investment casting alloys (platinum with 5 wt% ruthenium (Pt-5Ru) and platinum with 5 wt% cobalt (Pt-5Co)) suffer from poor castability and other drawbacks. In this work thermodynamic calculations of alloy properties were employed to optimise the alloy compositions. Segregation behaviour appeared to be important for the melting range. Scheil simulations were used to simulate segregation under typical casting conditions. Based on these simulation results, small additions of Co were found to significantly improve the castability of PtRu. Casting trials proved that ternary Pt-Co-Ru alloys show superior casting properties, in particular better form-filling and surface quality and reduced grain size and porosity compared to binary alloys. In order to replace Co, further work on other ternary systems appears necessary to study their melting range experimentally.

1. Introduction

The investment casting of platinum alloys is challenging due to their high melting temperatures and other physical properties (1), which promote crucible and investment reactions and limit the form-filling ability of the alloys. Platinum investment casting has been reviewed in the literature (2). Fryé *et al.* (3) studied the casting performance of the binary alloys Pt-5Ru and Pt-5Co. Pt-5Ru is the preferred alloy of many jewellery manufacturers, because it contains 100% platinum group metal (pgm), is non-magnetic and can be cast in air without oxidation. However, due to its high melting point, this alloy is very difficult to cast into filigree shapes. In addition it has a pronounced tendency to form micro-shrinkage porosity. Hot isostatic pressing (HIP) has been successfully used to reduce the residual porosity (4). Pt-5Co is a superior casting alloy for filigree items. The drawbacks of this alloy are its ferromagnetism, the potential oxidation of Co in air and the possibility that Co might be allergenic (5). Different platinum alloys have been studied for jewellery use (6), but alternatives to these simple binary alloys are currently limited.

The present study was carried out at the Research Institute for Precious Metals and Metals Chemistry (FEM), Germany, in collaboration with a group of German companies to better understand the investment casting of platinum alloys. The casting process was simulated using computational fluid dynamics (CFD) to help understand and optimise the relevant process parameters. The simulation was based on material parameters of the alloys, investment and crucible materials which were determined in advance. Selected casting trials were undertaken with optimised casting parameters. Based on sophisticated process control, the relevant process parameters were determined and

controlled in order to achieve reproducible casting conditions.

The present paper is divided into two parts. The first part (7) dealt with the evaluation of material properties, the casting simulation and the effect of process parameters on the casting result, in particular form-filling, surface quality and porosity of the cast parts. This paper presents the second part of the study. It describes the use of thermodynamic simulation for the optimisation of platinum alloys for investment casting. Based on equilibrium and non-equilibrium phase diagram simulations, the behaviour of the binary alloys was investigated and related to the casting process. Variations of the alloy composition resulted in a change of the thermodynamic properties such as melting range, segregation behaviour or energy release during solidification. By using and interpreting such information, alloy compositions with optimised casting properties were obtained and successfully tested in casting experiments. The potential of thermodynamic simulations has been demonstrated for gold and silver casting (8). Other industries have been using such simulation techniques successfully for many years (9). Elaborate thermodynamic databases have been developed for steels, aluminium, magnesium, titanium and nickel alloys (10). Due to the high material costs of precious metals the use of such simulation would help to develop new and superior alloys more cost effectively.

2. Experimental

Thermodynamic calculations were performed using the software Thermo-Calc V4.0 (Thermo-Calc, Sweden) and the software database SNOB3 (Scientific Group Thermodata Europe (SGTE) and Thermo-Calc, Sweden) which is dedicated to noble metal alloys (11). The software allows the calculation of multicomponent equilibrium phase diagrams based on assessed binary and ternary systems. The principle of thermodynamic simulation is the minimisation of the Gibbs free energy of the system as a function of temperature, pressure, composition and other selected variables. The CALPHAD methodology (CALculation of PHAse Diagrams) was introduced by Kaufman and Berstein in 1970 (12). It is based on a critical assessment of all available data (for example phase diagram, thermochemical data and *ab initio* data) of an alloy system (13). Each phase is described by a model that allows the calculation of its Gibbs free energy.

This function contains several interaction parameters determined by least squares fitting to the data and depends mainly on crystal structure, composition and temperature. Such assessment is usually done for binary and ternary systems. The idea is to obtain a comprehensive and consistent description of all phases, allowing the properties of multicomponent systems to be predicted. An example of a thermodynamic database for platinum-rich alloys is available in the literature (14).

The database SNOB3 that was used in this study was developed by the SGTE. It contains a description of the binary systems Pt-Co and Pt-Ru (**Figure 1**) and is recommended for calculations of platinum-rich alloys with small amounts of alloying elements. Very few ternary interaction parameters are available in the database. Therefore, the calculation of the ternary Pt-Co-Ru system was based only on binary interaction parameters. However, as binary systems are simple and do not have intermetallic compounds, this approach was deemed suitable.

Casting trials by centrifugal and tilt casting were made in order to demonstrate whether Co additions to Pt-5Ru improve the casting behaviour. Details of the experimental procedure, the casting parameters and the tree setup are given elsewhere (7). Evaluation criteria to assess the performance of the alloys were the form-filling of filigree items, the surface quality and the microstructure and porosity of the as-cast part. Vickers hardness measurements on as-cast samples were carried out according to a standard procedure (15) with a load of 1 kg (HV1). At least three measurements on at least two samples per composition were made. The values and uncertainty ranges (standard deviation) given in **Table I** are the average of at least six measurements per composition.

3. Thermodynamic Simulation Results

Figure 1 shows the Pt-rich side of the binary systems Pt-Co and Pt-Ru, which are the basis for the most common jewellery alloys Pt-5Co and Pt-5Ru. The Pt-Co system shows complete solubility in the solid and liquid phases and a minimum melting temperature at about 50% Pt (16). The addition of Co to Pt results in a significant reduction of the melting point, about 100ºC for 5 wt% Co. The melting range at 5 wt% Co is relatively small and only about 15ºC (**Figure 1**). The binary Pt-Ru system shows a peritectic reaction on the Ru-rich side involving the hexagonal (Ru) phase. Ru increases the melting point by about 50ºC for 5 wt% of Ru. The melting
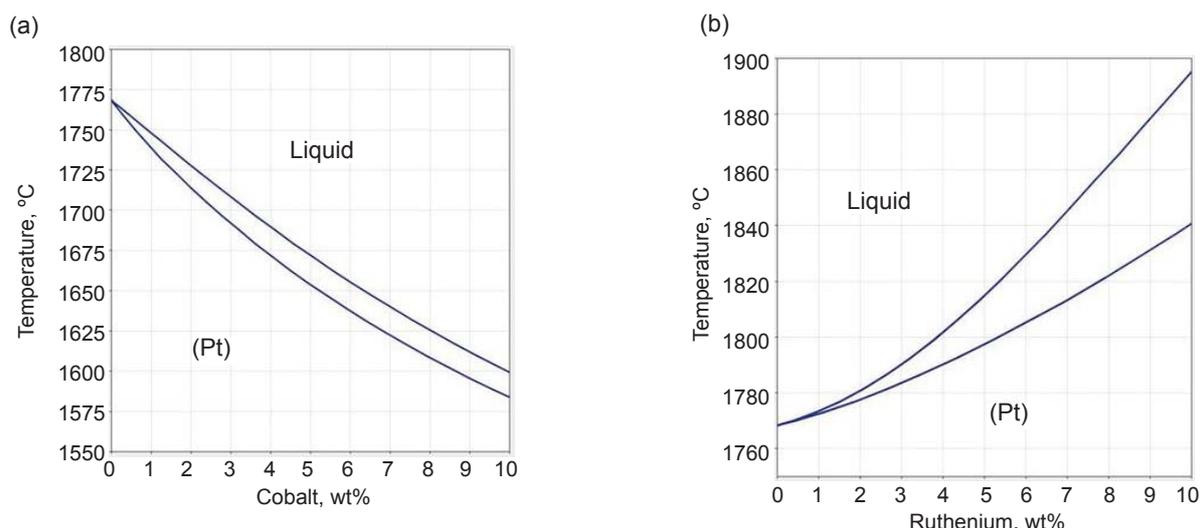
Fig. 1. Calculated binary phase diagrams of: (a) Pt-Co; and (b) Pt-Ru systems

Table I Vickers Hardness Measured on Metallographic Cross-Sections of As-Cast Double-Gate Rings				
Alloy	**Pt-5Co**	**Pt-3.5Co-1.5Ru**	**Pt-1.5Co-3.5Ru**	**Pt-5Ru**
Vickers hardness, HV1	129 ± 4	126 ± 4	129 ± 6	129 ± 6
Melting enthalpy[a], J g^{-1} K^{-1}	121	121	124	122

[a]*The melting enthalpy was calculated by Thermo-Calc*

range of ~15ºC is similar to that of Pt-5Co. It should be noted that the original data on the Pt-Ru system are limited to the melting points of the pure elements and the solidus and liquidus temperature of two binary alloy compositions (17). Hence, the solidus and liquidus line (16) are given as dashed lines. The thermodynamic calculations fit reasonably to the experimental data, but further experimental investigations are required for the binary Pt-Ru system.

The calculation of the ternary Pt-Co-Ru system was based on extrapolation from the binary systems. No experimental data of the ternary system were found in the literature. **Figure 2(a)** provides the calculated liquidus (red lines) and solidus surface (blue lines) in the Pt-rich corner. For alloys with a Pt content of 95%, a vertical section has been calculated (**Figure 2(b)**). With increasing Co content, liquidus and solidus temperatures are lowered. The solidus and liquidus lines are nearly parallel, i.e. the melting range of alloys with the composition Pt$_{95}$Co$_x$Ru$_{5-x}$ is nearly constant.

The thermodynamic simulations presented so far are valid for the equilibrium condition, however this is not applicable to investment casting processes. Usually

segregation of the lower melting component occurs into the interdendritic regions during cooling, resulting in a depletion of the component with higher melting temperature and hence a reduction of the solidus temperature. McCloskey and Aithal (18) investigated the segregation in Pt-5Ru and Pt-5Co and compared experimental results with thermodynamic simulations. The melting point of pure Pt is lower than that of Pt-Ru and this limits possible segregation, because segregation beyond pure Pt cannot occur. Therefore, the experimentally observed non-equilibrium melting range of Pt-5Ru was only 30ºC, while it was ~175ºC for Pt-5Co under similar casting conditions. The higher non-equilibrium melting range is supposed to be the reason for the better casting characteristics of Pt-5Co.

The green tie lines in **Figure 2(a)** connect the solid and liquid phases in thermodynamic equilibrium during solidification. If Ru is replaced by Co in alloys with 95% Pt, the orientation of the tie lines, i.e. the direction of segregation, changes. The composition of the melt moves towards pure Pt since at a given temperature, the Pt-rich side of the solid-liquid two-phase region is still liquid while the Ru-rich side solidifies. Small
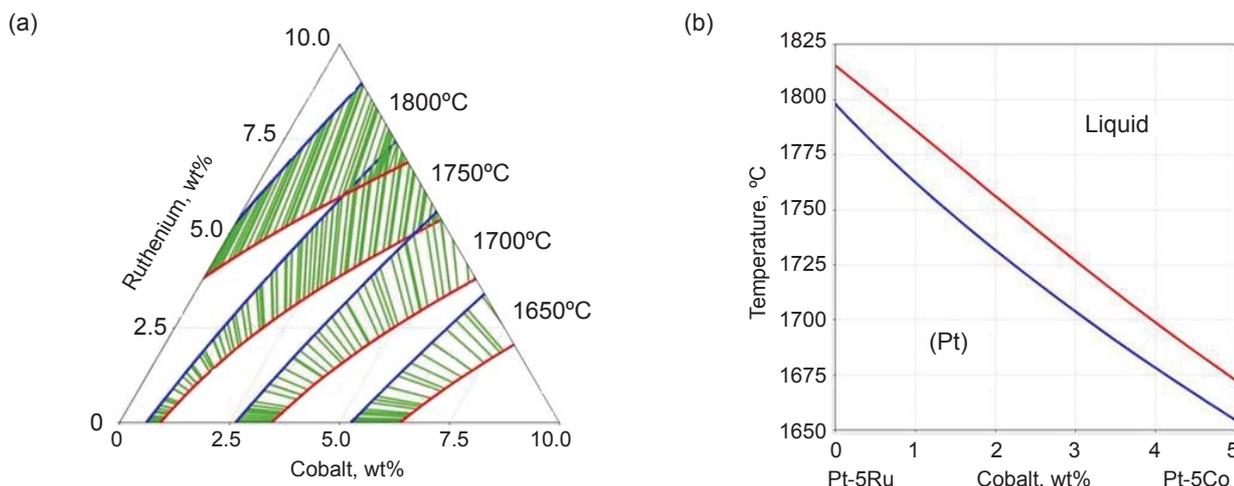
Fig. 2. (a) Liquidus (red) and solidus surface (blue) of the ternary Pt-Co-Ru system; (b) vertical section at 95% platinum

additions of Co change the direction of segregation in the ternary system, i.e. the melting interval is increased by segregation and is no longer limited by the melting point of pure Pt.

The extent of segregation under real casting conditions can be simulated by the Thermo-Calc software in the so-called Scheil module. The Scheil calculations in **Figure 3**, which are taken into account for the segregation, show the non-equilibrium melting range of some binary and ternary alloys. The replacement of Ru by Co results in a significant increase of the melting range of the ternary Pt-RuCo alloys compared to binary Pt-5Ru. The melting range of the ternary alloys under non-equilibrium solidification is approximately constant for the different calculated Co contents shown in **Figure 3(a)**. Associated with the segregation is a non-uniform/inhomogeneous composition of the cast product. **Figure 3(b)** shows the composition of the solid phase precipitate at a certain temperature. According to the orientation of the tie lines, Pt segregates to the liquid phase in Pt-5Ru. Therefore, the primarily solidifying dendrite cores have a low Pt concentration, which increases towards the surface of the dendrites. The Pt content in the dendrite varies between 93% at the onset of solidification and 98% at the end of solidification.
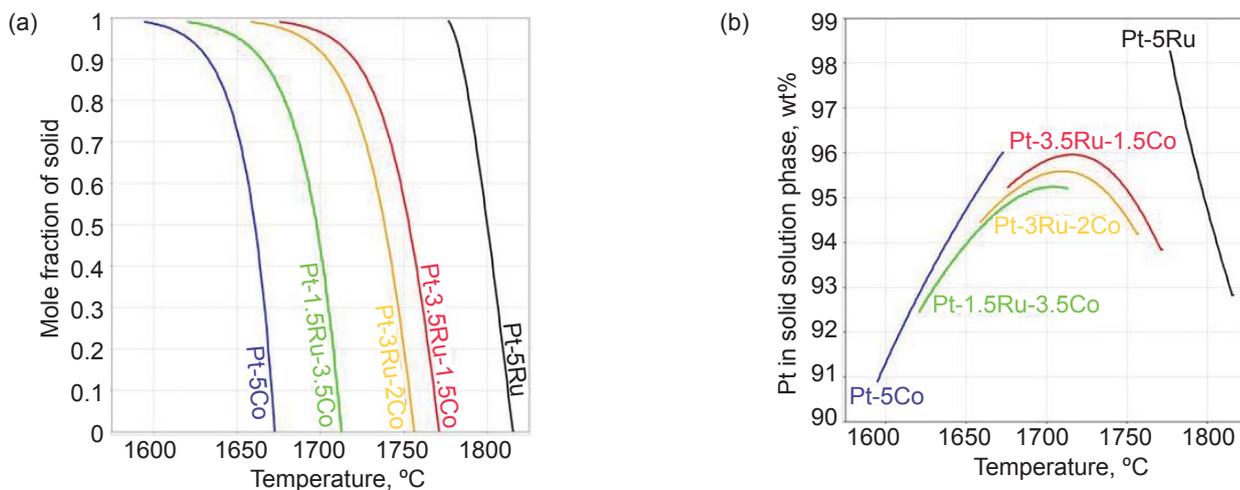

Fig. 3. Scheil calculation of: (a) the phase fraction of liquid; and (b) the composition of the platinum solid solution phase (FCC_A1) as a function of temperature

For the ternary alloys, a gradual change in segregation behaviour occurs as Ru is replaced by Co, as described by the tie line orientation in **Figure 2(a)**. As a consequence, the composition of the as-cast microstructure supposedly becomes more homogenous for ternary alloys. Alloys with 2% Co and 3% Ru show a nearly constant dendrite composition of 94–95% Pt throughout the solidification (**Figure 3(b)**). At higher Co content the segregation direction changes, i.e. Pt shows no segregation to the dendrites. Hence, Pt is enriched in the dendrite cores and depleted in the interdendritic areas. For Pt-5Co, the concentrations of Pt are 96% and 91% at the beginning and at the end of solidification, respectively.

Qualitative energy-dispersive X-ray (EDX) spectroscopy mappings of the platinum distribution for three selected alloys (Pt-5Ru, Pt3.5Co-1.5Ru and Pt-5Co) are shown in **Figure 4**. The brightness level of the image is proportional to the platinum content, which is high in the bright areas and low in the dark areas. The segregation is most pronounced for Pt-5Ru. Platinum-poor dendrite cores are clearly visible in the elemental map. Pt-5Co shows platinum-rich dendrites that are larger than those seen in Pt-5Ru. Therefore the concentration gradients are less steep in the dendrite cores. The ternary alloy

Pt-3.5Co-1.5Ru shows no pronounced segregation of platinum. A good correlation between the non-equilibrium Scheil simulation in **Figure 3(b)** and the experimental findings was observed.

4. Casting Results
4.1 Form-filling

Standard grid patterns were mounted at the tip of a casting tree with ~150 g metal weight. The dimensions of the grid were 29 × 23 mm (length × width). The mesh had a rectangular cross section of 0.8 × 1.0 mm (**Figures 5** and **6**). As expected from previous studies (2) Pt-5Co showed much better form-filling than Pt-5Ru. Complete grid-filling was obtained by both casting methods for Pt-5Co, while the grid was only ~20% filled for Pt-5Ru. Tilt casting resulted in slightly less form-filling compared to centrifugal casting. If Ru was partially substituted by Co, the form-filling increased significantly. In centrifugal casting, minor substitutions resulted in significant improvement in form-filling as can be observed in **Figure 5(b)** for 0.7% Co. When the Co content exceeded 1.5%, complete grid-filling could be achieved by centrifugal casting. Tilt casting, on the other hand, only resulted in complete form-filling at a Co content of at least 3.5%.
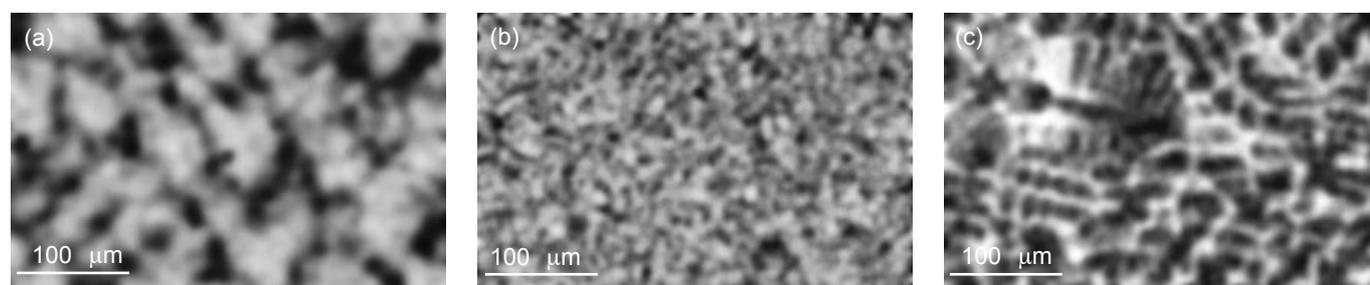

Fig. 4. SEM-EDX elemental maps of the distribution of platinum in the as-cast condition for three different alloys: (a) Pt-5Co; (b) Pt-3.5Co-1.5Ru; (c) Pt-5Ru
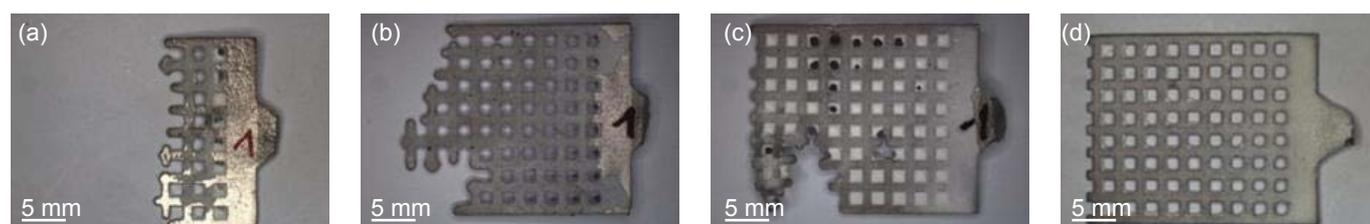

Fig. 5. Form-filling of a test grid in centrifugal casting as a function of alloy composition: (a) Pt-5Ru; (b) Pt-0.7Co-4.3Ru; (c) Pt-1.5Co-3.5Ru; and (d) Pt-5Co
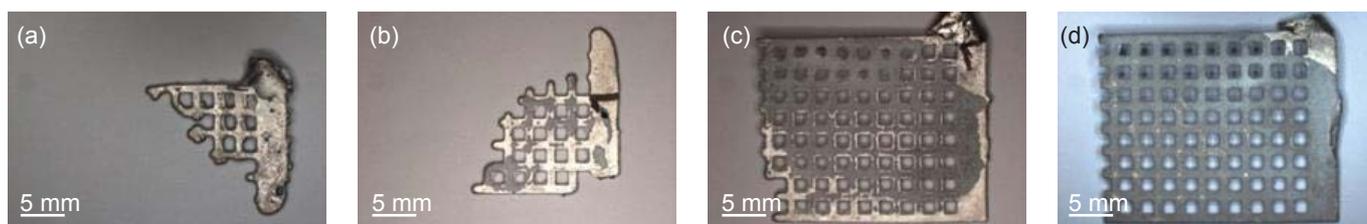
Fig. 6. Form-filling of a test grid in tilt casting as a function of alloy composition: (a) Pt-5Ru; (b) Pt-1.5Co-3.5Ru; (c) Pt-3.5Co-1.5Ru; and (d) Pt-5Co

4.2 Surface Quality

The surface quality was evaluated for a given phosphate bonded investment and a standard ring pattern with thin and thick cross section areas. The available investments produce fairly significant differences in surface quality (7). Especially heavy sections are prone to cause investment breakdown for some commercially available materials. For the present study, an investment was chosen that provided good surface quality for Pt-5Co, but showed investment breakdown in heavy sections for Pt-5Ru. The mechanism of investment breakdown is explained in detail in Part I (7). **Figures 7(a)–(c)** show macroscopic images of the selected rings. Detailed scanning electron microscopy (SEM) images were taken from the surface of the thick, flat section close to the sprues (**Figures 8(a)–(c)**). At this position, the surface was very rough for the Pt-5Ru part, while a smooth surface was obtained in the thin sections of the ring. Pt-5Co showed a smooth surface over the entire ring. The substitution of Ru by Co improved the surface of the ring in its thick sections. With 1.5% Co a surface quality nearly as good as that of Pt-5Co was obtained. Higher Co contents resulted in further improvement. Similar surface quality results were obtained for both casting methods.

4.3 Microstructure and Porosity

Metallographic samples were prepared by standard metallographic techniques. Grinding was done by

Fig. 7. Macroscopic images showing the surface of as-cast rings of 95% platinum alloys: (a) Pt-5Ru; (b) Pt-1.5Co-3.5Ru; and (c) Pt-5Co
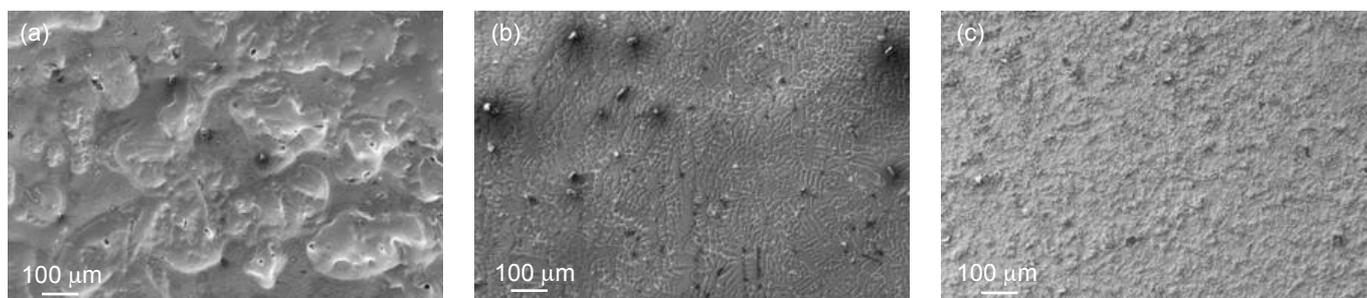

Fig. 8. SEM-SE images showing the surface of as-cast rings of 95% platinum alloys: (a) Pt-5Ru; (b) Pt-1.5Co-3.5Ru; and (c) Pt-5Co

successively employing silicon carbide paper down to 1200 grit followed by polishing with diamond suspension of 6 μm and 3 μm. The standard preparation leaves a thin deformed surface layer which is impossible to avoid during grinding and polishing of relatively soft metals like Pt. Therefore, a final polishing step was performed by ion beam milling using two argon ion guns at an angle of 1.5º. The sample was rotated to achieve homogenous polishing. Such ion polishing removes the deformed surface layer and reveals micro-porosity, which is usually obscured by the surface deformation when using conventional sample preparation. Finally, the polished samples were investigated without further etching by SEM using back-scattered electrons. The electron channelling contrast in back-scatter SEM-imaging shows different grain orientations at different brightnesses.

The microstructure of the prepared samples is shown in **Figure 9**. The metallographic sections were made in the ring plane. The area shown in **Figure 9** was observed in the thick section of the ring, which was most prone to shrinkage porosity. The Pt-5Ru ring had many small pores of up to 10 μm in size. The shape and interdendritic position of the pores indicate that such pores were formed at the very end of solidification when further feeding was no longer possible. Micro-shrinkage pores and small grain size are typical for Pt-5Ru in the as-cast condition (3). Additional sprues were not sufficient to avoid micro-shrinkage. The effect of casting conditions, heat treatment and HIP on microstructure and porosity of the most common binary Pt alloys is described in detail elsewhere (4, 7). Pt-5Co showed no such micro-shrinkage, but had a much larger grain size compared to Pt-5Ru. Therefore neither alloy shows an ideal microstructure, which would be fine grained and free of porosity.

In the present study the substitution of Ru by small amounts of Co helped to avoid micro-shrinkage. Even small additions of 0.7% Co were sufficient to significantly reduce the porosity, while the grain size remained comparable to Pt-5Ru. ~1.5% Co was necessary to fully avoid micro-shrinkage (**Figure 9(b)**). With increasing Co content, the grain size gradually increased. Typical hardness values for some binary and ternary alloys are given in **Table I**. No significant difference in hardness was observed.

5. Discussion

The replacement of 1–3% Ru in Pt-5Ru by Co resulted in a significant improvement of form-filling, surface quality and microstructure during investment casting. The better form-filling could be explained by a lowering of the solidus and liquidus temperatures of the ternary alloys. However, the melting range of the binary and ternary alloys was very similar. Taking into account segregation during non-equilibrium solidification provided a better understanding of the improved form-filling. The direction of segregation changed even for very small additions of Co, i.e. the melting point of pure Pt was no longer a limitation for the end of solidification. This gave more time for the flow of the semi-solid metal during casting. With increasing Co content the castability of the ternary alloys became similar to Pt-5Co. Depending on the casting process 1.5% Co (centrifugal casting) or 3.5% Co (tilt casting) were required for complete form-filling under the chosen casting conditions.
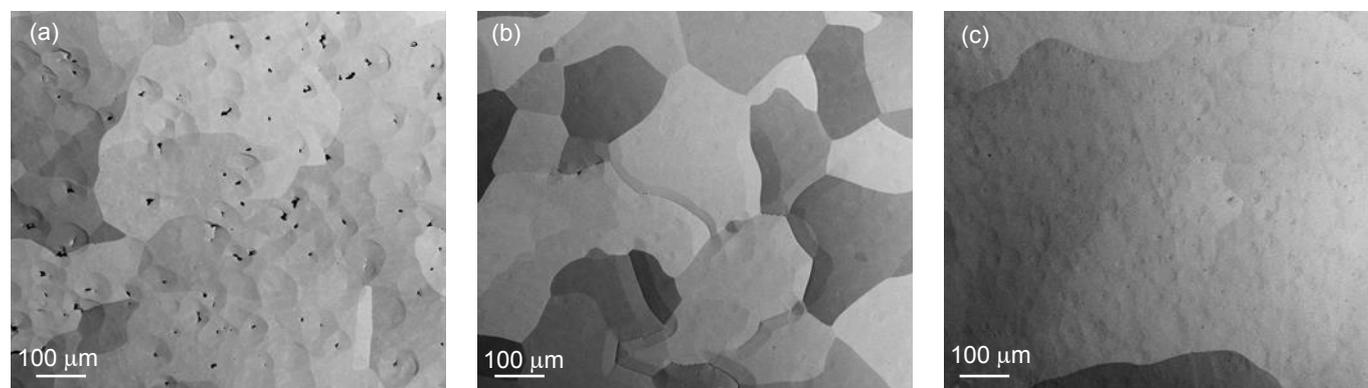

Fig. 9. SEM-BSE images showing the microstructure and porosity of 95% platinum alloys: (a) Pt-5Ru; (b) Pt-1.5Co-3.5Ru; (c) Pt-5Co

The improved surface quality is also related to the temperature range of solidification. The lower temperatures reduced the risk of investment breakdown. A further factor was heat release from the alloy during solidification. The amount of heat released during solidification is equal to the enthalpy change (melting enthalpy, ΔH_M). Values for the different alloys were calculated under equilibrium conditions and are given in **Table I**. All binary and ternary alloys showed a very similar melting enthalpy, i.e. the heat released during solidification was approximately equal for all alloys. However, if non-equilibrium solidification is considered, the situation changes. **Figure 10** provides the apparent heat capacity of selected alloys as a function of temperature. The apparent heat capacity, $C_{p,app}$, is the slope of the enthalpy curve at a certain temperature. According to **Figure 10**, the heat release during solidification differs between Pt-5Ru and the Co containing alloys. In Pt-5Ru $C_{p,app}$ remains relatively high at the beginning of solidification, i.e. much heat is released at a very high temperature. As solidification proceeds, $C_{p,app}$ decreases quickly. This means that the investment is highly stressed at high temperature and the risk of investment breakdown increases. If the Co-content is increased, $C_{p,app}$ quickly decreases with decreasing temperature from the onset of solidification. Hence, the temperature range in which energy is released is much smaller. Towards the end of the solidification the slope of the $C_{p,app}(T)$ curve becomes very small. Surface quality was found to be independent of the applied casting procedure.
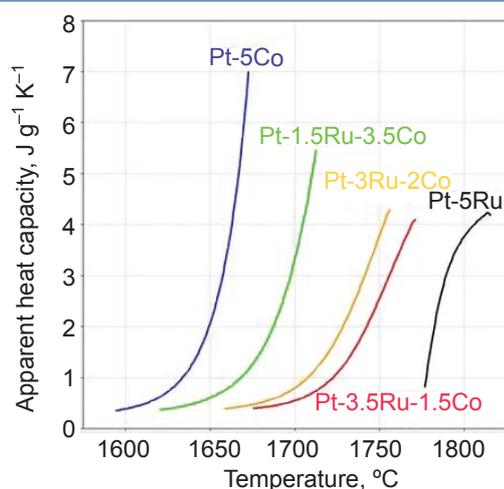

Fig. 10. Scheil calculation of the apparent heat capacity during solidification

An important drawback of Pt-5Ru was the formation of micro-shrinkage pores throughout the entire cast piece. Small Co additions reduced this effect significantly. As described above, Co increased the solidification interval and thereby enabled feeding for a longer time. **Figure 10** also shows that in Co containing alloys more heat was released towards the end of the solidification over a relatively broad temperature range, which should keep the alloy longer in the semi-solid state and thereby improve feeding at this critical step of form-filling. The cooling rate during casting was also found to be critical for the occurrence of micro-shrinkage. In a comparative study of tilt and centrifugal casting, the cooling speed was slower for tilt casting. This was not so much a factor of the casting method, but of the construction of the particular machines. Slower cooling in the tilt casting machine made it possible to avoid micro-shrinkage even for Pt-5Ru (7).

6. Summary and Conclusions

Ternary Pt-Co-Ru alloys are currently not available on the market. In view of the drawbacks of Co, including its magnetism and the suspicion that Co could be allergenic, further alloy development, and especially the experimental investigation of melting ranges, is required. Very little and sometimes contradictory thermophysical data are available in the literature, even for pure platinum (19) and this deficiency needs to be addressed, in order to investigate whether Co could be completely replaced by other alloying elements.

Thermodynamic simulations were used in order to better understand the behaviour of the widely used jewellery casting alloys Pt-5Ru and Pt-5Co and to develop alloys with improved castability. The addition of Co to Pt-5Ru lowered the equilibrium solidus and liquidus temperatures meaning that lower casting temperatures were required. Non-equilibrium calculation showed a change of the segregation direction and thereby a significant increase of the melting interval. The improved casting performance of the ternary alloys could be explained by the alloy thermodynamics, i.e. the heat release as a function of temperature during solidification.

Casting trials demonstrated that small additions (1–2%) of Co to Pt-5Ru significantly improved form-filling and surface quality. Micro-shrinkage could be avoided while small grain size was maintained. The chemical homogeneity of the ternary alloys was

improved compared to the binary alloys. The hardness was not altered by the Co addition. The required Co content to obtain optimised form-filling depended on the casting method and was about 1.5% and 3.5% for centrifugal and tilt casting, respectively.

Acknowledgements

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