This paper provides a database of mechanical properties for most of the commercially available platinum alloys currently in use for jewellery purposes. The alloys were tested for mechanical properties through tensile and microhardness testing in the as-cast and hot isostatically pressed conditions. Microstructural characterisations were performed using scanning electron microscopy (SEM).

1. Introduction

There is scant data available in the literature evaluating fitness for purpose of platinum alloys used in the creation of jewellery designs (1–8). Only recently has literature on basic properties of platinum jewellery alloys been published (9, 10). In an industry steeped in tradition and ruled by millennia of hands-on experience, this fact is not surprising. Rather, a substantial body of tribal knowledge exists concerning what does and does not work and for many years this was largely sufficient. Enter the digital revolution where cast versus hand-fabricated products now dominate and tribal knowledge alone is no longer enough. This is true because the two methods of production result in very different material properties and this difference can affect the end consumer’s experience when it comes to wear resistance. Take, for example, the common platinum-iridium alloy Pt90-Ir10. This alloy was used to create much early 20th century platinum jewellery and a good amount of this jewellery is still in circulation today. And though purely anecdotal, there is substantial evidence that such platinum estate jewellery has stood up quite well to the test of time, remaining strong and resilient despite decades of daily wear. But is this still the case when legacy alloys used in hand fabrication are used to make jewellery in a purely cast form? In past eras when the vast majority of platinum jewellery was hand fabricated, the metal was bent, formed, twisted, compacted and hammered into the desired shape. All of these hand-working methods introduce work hardening, a mechanism by which the hardness and strength of the metal is increased through deformation of the crystal lattice. Consequently, most hand-fabricated platinum jewellery tends to be inherently strong. Contemporary jewellery designs, on the other hand, are almost entirely produced through casting and not likely to experience the benefits of work hardening. Therefore, platinum alloys that were once viewed as robust are now found to be lacking in their cast forms. Given that today the labour savings achieved through casting near net-shape jewellery is nothing less than an economic imperative, it is necessary to take a closer look at platinum alloy choices to determine suitable strength levels for cast product.
In order to reach an understanding of alloys that meet fitness for purpose, we must first create data that will characterise mechanical properties for mainstream alloys used globally. In the present work we explore the key characteristics of strength, ductility, microstructure and porosity levels. Earlier works by Fryé and Fischer-Bühner (11) and Fryé et al. (12) reported the effects of hot isostatic pressing (HIP) of platinum alloy castings on mechanical properties and microstructures. The present work increases the number of alloys covered with the goal of building a comprehensive database for platinum jewellery alloys used globally. The present data also includes castings both with and without HIP in order to augment the comparison of metallurgical quality between the two conditions.

2. Experimental

2.1 Alloys Tested

The alloys in Table I were selected for testing based upon their prevalent use in the United States,
Europe, China, Japan and India. Pure platinum only has a Vickers hardness (HV1) of about 50 HV1 and can be hardened by solid solution hardening when alloyed. The effectiveness of different alloying elements in their annealed condition is published elsewhere (13–15). Gallium containing alloys are known and have been used for some time. Recently, indium containing alloys were developed, such as 95Pt-Au-In (16).

In this work we categorised the alloys according to the effectiveness of the alloying elements into three groups for a given platinum content of either 90 mass% or 95 mass%. Soft alloys (<120 HV1 at 5 mass% to 10 mass%) are obtained by alloying with rhodium, copper, copper-cobalt, palladium-cobalt and iridium. Medium-hard alloys (120–150 HV1 at 5 mass%) are possible with the addition of ruthenium and cobalt. Finally, hard alloys with a hardness above 150 HV1 at 5 mass% are achieved by alloying with Ga and In in addition to Ru, Cu, Co or Au. Actual hardness depends on the casting condition. Alloys that contain Co are just at the threshold from soft to medium-hard.

All alloys were cast under comparable conditions using a flask temperature of 850°C. The casting temperature was chosen according to the melting range and varied between 1850°C for the lowest melting alloy (95Pt-Co-In) and 1960°C for the highest melting alloy (90Pt-10Rh). Details on the investment casting and HIP processes are provided elsewhere (11, 12, 17).

2.2 Mechanical Testing and Hardness Measurement

Tensile testing was performed according to DIN EN 10002-1:2001-12 in a universal testing machine (ZwickRoell Z100HT) at a temperature of 23±5°C using the test bar geometry shown elsewhere (18). The preparation of the samples for testing was done based on the international standard ISO 22674:2016. The standard describes the testing of cast alloys for dental applications. It requires the valid testing of at least four samples out of a set of six samples. We used four samples for testing and all samples passed the test according to ISO 22674:2016. According to ISO 22674:2016 samples should be tested with their as-cast surface after removal of casting beads and fins. The surface finish in this work was as-cast with the exception of a light bead blast for complete ceramic shell removal. We inspected for any fins or positives and any found were very lightly touched with emery paper. We were careful not to work the surfaces very much. The strain was measured until fracture using a strain gauge on a starting length of 15 mm. The testing speed was 1.5 mm min\(^{-1}\) until the 0.2% proof stress was surpassed and then increased to a strain-controlled strain rate of 0.0025 s\(^{-1}\). The values for 0.2% proof stress (YS), ultimate tensile strength (UTS), elongation (\(\varepsilon_f\)) and reduction of area (ROA) were determined on four samples each in the as-cast and HIP conditions. Vickers microhardness (diamond pyramid hardness, HV1) was measured on metallographically polished plates and half shanks using a load of 1 kg.

2.3 Metallographic Preparation

The test geometry used for this purpose was a half-shank ring (12). The half-shanks were split longitudinally along the centreline and embedded in epoxy resin. The interior surface was then ground with silica sandpaper in successively decreasing grit sizes, followed by polishing with diamond paste at 15 µm, 6 µm and 1 µm. This process requires considerable operator diligence due to the softness of some alloys. Soft alloys tend to smear during grinding and polishing and pores can be easily closed, which can result in artificially low porosity values. An example showing the effect of polishing quality can be seen in a previous publication (19). To further avoid artefacts from polishing, an additional ion-polishing step was done that removed the deformed surface layer to obtain optimum image quality.

Metallographic samples were investigated by SEM using the back-scattered electron detector. The contrast of the image is caused by local differences in composition and therefore allows segregation phenomena to be identified.

3. Results

3.1 Microhardness Testing

Results of hardness testing are given in Table I. Data from earlier work (18) are also included in Table I for comparison purposes. The alloys containing Cu-Co, Pd-Co, Rh, Ir, Ru or Co as the sole alloying elements show only solid solution hardening and are therefore relatively soft. The softest and most ductile alloys are those containing Ir and Rh as alloying elements (95Pt-5Ir, 90Pt-10Ir and 90Pt-10Rh). Alloys containing Co and Ru are slightly harder because these elements are more effective hardeners (13). The addition of elements such as Ga and In results in even more
effective solid solution strengthening and can furthermore result in precipitation hardening due to the formation of Pt₂In and Pt₂Ga precipitates, respectively, if a certain amount of Ga or In is exceeded. Precipitation hardening is very sensitive to temperature history and requires a two-step heat treatment for optimum properties, but this type of heat treatment was not done in the present study. It may also take place to some extent during the slow cooling phase (~800°C down to 300°C), which is distinguished from and follows the rapid solidification after casting. In any event, cooling conditions may play a strong role here.

Hardness is generally proportional to UTS values, but it does not provide information about the ductility of alloys. Such information is generally obtained through tensile testing, which comprises the section that follows.

For two of the alloys (95Pt-5Ru and 95Pt-5Co) larger data sets from a previous study existed (20). This allowed a statistical analysis of many as-cast samples. For 95Pt-5Ru 88 hardness tests on 24 as-cast samples were evaluated that provided an average value of 129 HV1 with a standard deviation (σ) of 4 HV1. Table I provides the average and a confidence interval of ±2σ for these two alloys. Over 95% of all measurements lie in this range.

### 3.2 Tensile Testing

Table I provides average values of four tensile test samples and data on Vickers hardness measurements. Details on measurement conditions are provided elsewhere (12). The fracture surface for each test bar was inspected using a stereomicroscope to identify casting defects (shrinkage pores). A limited number of samples were found to have casting defects and these test results were excluded from the averaging. It is worth noting that although material properties of as-cast platinum alloys are scarcely available in literature (9, 10, 21), the little data that are available for 95Pt-5Ru and 95Pt-5Co showed very good correlation with our data (22).

Work hardening describes the increasing strength of a material with increasing plastic deformation. Plastic deformation happens through dislocations, which are lattice imperfections that allow the movement of atoms under a plastic strain. With increasing strain, the number of dislocations increases and adjacent dislocations hinder one another’s movement, making the material stronger. As a consequence, higher stress is required for further straining. This is reflected by the higher level of UTS (the endpoint of uniform deformation) compared to 0.2% proof stress (the beginning of deformation).

The elongation (ε) is the maximum deformation that a sample can take until it fractures and the ROA value provides information about the necking or contraction of the sample once stresses above UTS have been applied. A detailed description of these four values determined from tensile testing is provided in our earlier work (17).

Alloys containing Co, Ga and In show higher strength and lower ductility. In particular, work hardening increases compared to the simple binary alloys containing Ru, Ir or Rh. The alloys containing Cu, Pd-Co and Ir are the softest and most ductile of the group and show a lesser amount of work hardening, making them easier to deform during bench operations. One curiosity occurs with the Cu containing alloys that is worth noting: after HIP the work hardening increases significantly compared to the as-cast condition. This effect is due to a reduction in the 0.2% proof stress as hardness and UTS are unchanged by HIP.

HIP significantly reduces the scatter of results among the four samples of each series, as discussed in detail in our earlier paper (11). The strength values YS and UTS are only slightly affected by HIP, with a small but negligible increase observed for most alloys. The effect of HIP is much stronger on the ductility values ε and ROA and is most pronounced in the ROA value. This effect of HIP on ROA is attributed to a reduction in porosity that results from the process. Some alloys such as 95Pt-5Ir, 90Pt-10Ir, 95Pt-5Co, 95.5Pt-3.5Ru-1Co and 95.5Pt-3Pd-1.5Co show a lesser effect on ROA after HIP because they already exhibit lower levels of porosity in the as-cast condition. The increase of the ROA was most pronounced for the hard alloys 95Pt-Ru+ and 95Pt-1.8Au-2.7In-0.5Ru (16). Only one alloy, 95Pt-2Cu-3Ga, shows a reduction in the strength and ductility levels after HIP, although this result is based upon limited data due to the omission of two of the four samples due to casting defects.

### 3.3 Microstructures

The objective of the microstructural investigation was to identify porosity and determine grain size. For selected alloys the microstructure in the thicker end of the half-ring shanks is shown, both in the as-cast and HIP conditions in Figure 1 and Figure 2. During investment casting the material solidifies by forming dendrites with a dendrite spacing of
Fig. 1. (a) and (c) 95Pt-Ru-Ga+ in the as-cast condition; (b) and (d) 95Pt-Ru-Ga+ in the HIP condition. Dendritic structures inside the grains are visible before and after HIP.

Fig. 2. (a) and (c) 90Pt-10Ir in the as-cast condition; (b) and (d) 90Pt-10Ir in the HIP condition.
ca. 40 µm. This forms typical columnar grains from the surface that meet in the centre of the part. This appearance is most obvious for the Pt-Ir alloys (Figure 2). Other alloys show more globular (often called equiaxed) grains. Whether globular or columnar grains form depends on alloy composition, but also on casting parameters such as melt and flask temperatures. In particular, the melt temperature is more challenging to control and may vary from one pour to another. Therefore, the resulting microstructure (globular or columnar) may differ from one casting to another for the same alloy as in Figure 1.

The shape of the dendrites depends on the alloy chemistry. A detailed documentation of the microstructure is provided in (17). Alloys containing low melting additions such as Ga tend to have more pronounced dendrite formation (Figure 1). As dendrites grow they come into contact with each other and isolated volumes of liquid metal remain in between them. As soon as the solid fraction reaches 50–60 vol% further feeding by the melt is no longer possible. The isolated volumes of liquid metal shrink by 4–5 vol% during solidification (9) and as a result small scattered pores remain (seen as micro-shrinkage pores), often referred to as casting porosities. Such micro-shrinkage porosity is observed in all alloys that contain Ru, Ga or In (Figure 1(c)). The porosity is most pronounced in thicker sections such as the wide end of the ring shank.

The effect of alloy composition on micro-shrinkage porosity in 95Pt-5Ru-based alloys is described in detail in (23, 24). Binary 95Pt-5Ru showed excessive micro-shrinkage pores located between the dendrites. The addition of small amounts of Co changes the segregation direction from the binary system to the ternary system and thus results in a reduction of micro-shrinkage pores. In the case of shrinkage porosity, most pores are isolated from the surface and do not contain any appreciable amount of gas, therefore HIP is a useful mechanism for healing them. The external gas pressure applied during HIP acts on material that is soft at high temperature. The internal pores are collapsed and bonded during HIP, leaving a fully dense microstructure under ideal conditions. The effectiveness of HIP is demonstrated by images of the microstructure taken following HIP that are essentially free of pores. This can be seen by comparing Figure 1(c) with Figure 1(d) and Figure 2(c) with Figure 2(d).

A third feature of interest is segregation. Segregation means a change in the chemical composition of the melt during solidification. Under ideal conditions, the cast object should have a homogeneous composition after solidification. However, this involves diffusion processes that require a certain amount of time that is not provided for in Pt alloys, which by nature solidify very quickly under typical casting conditions. As a consequence, the high melting elements of the alloy concentrate in the dendrite cores while the lower melting elements concentrate in the remaining melt. The actual segregation can be obtained from phase diagrams and depends on the cooling rate and alloy composition. Low melting elements such as Ga or In that were added to some alloys in this study showed strong segregation to the liquid phase. These elements therefore concentrate in the interdendritic regions. The inhomogeneous composition of the cast part is shown most clearly in Figure 1 by the different shades of grey inside the grains. The dendrites appear bright in back-scattered electron images, because they are rich in elements of high atomic mass, namely Pt and Ru that precipitate first from the melt. The elements of low atomic mass that concentrate in the interdendritic regions make these regions appear darker. The segregation appears to be unaffected by HIP (18). It was demonstrated by thermodynamic simulations that the segregation depends strongly on the curvature of the liquidus and solidus surface (24).

The grain size of the alloys was determined by the SEM images. Grain size depends on the actual cooling conditions, which might be slightly different from one casting to another as described above. Grain size further depends on the exact position of the metallographic section, especially on the distance of the section from the surface of the part. The position might differ by ±0.2 mm from sample to sample. With this caveat in mind, general trends in grain size were observed with most alloys showing a relatively coarse grain size in the range of 0.5–1 mm. The Pt-Ir alloys tend to be at the upper end of this range. Smaller grain size in the range of 100–300 µm is observed for some alloys including 95Pt-5Ru, the 95Pt-Ru-Ga alloys and 95Pt-4Co-1In. A general trend that the addition of Ga or In results in smaller grain size was not observed. Lastly, it is unknown whether micro-alloying was used by the manufacturers to reduce the grain size in some of these alloys.
4. Discussion

4.1 Correlation of Hardness and Microstructure

The alloys containing Ga or In showed significantly higher hardness and strength compared to the binary alloys. This is a result of effective solid solution strengthening and maybe also of age hardening by the precipitation of the intermetallic phase Pt$_3$Ga or Pt$_3$In (22). The identification of precipitates would require high resolution transmission electron microscopy studies, which is beyond the scope and possibilities of this study. However, considerations based on phase diagrams and thermodynamic simulations were used in order to assess the possibility of precipitation hardening in the investigated Pt-Ru-Ga alloys. These results were linked to microhardness testing results obtained from dendrites and interdendritic regions as described below.

Figure 3 shows the temperature-concentration (isopleth) section of the Pt-Ru-Ga system at 95 mass% platinum. In Figure 3(a) and Figure 3(b) the compositions 95Pt-5Ru and 95Pt-5Ga are shown, respectively. The exchange of Ru by Ga reduces the liquidus and the solidus temperatures. At Ga content above 4.5% the binary eutectic reaction $L \rightarrow (Pt) + Pt_3Ga$ is reached at a temperature of 1356°C. This is slightly below the binary eutectic temperature of 1361°C (22). Alloys with Ga content above 2.2% should show the precipitation of Pt$_3$Ga upon slow cooling from high temperatures or ageing above 600°C. The In containing alloys show a similar behaviour, but the eutectic reaction is observed at higher In contents. For the alloys investigated in this study the Ga content is far below 4.5%. In any case, the eutectic reaction can be observed in alloys with lower Ga content due to segregation of Ga in the liquid phase. The segregation was calculated for two alloys with typical Ga content using the Scheil module of the Thermo-Calc® software package (Figure 3(b)). The solid lines provide the maximum segregation, while the dashed lines show the equilibrium solidification according to the phase diagram (Figure 3(a)). As can be seen from the diagram the eutectic reaction is likely to occur at Ga contents of 2.5%. This would result in significant hardening, especially after slow cooling of the flask following casting.

The metallographic images (Figure 1) show the segregation at higher magnification. Based on the thermodynamic considerations for segregation it can be expected that the hardness of the interdendritic regions, where Ga is concentrated, will be higher compared to the dendrite cores where Ga content is low. Due to the size of the interdendritic regions it is very difficult to make hardness measurements in different areas. Therefore, a matrix of 10×10 hardness indents with a distance of 50 µm between indents was measured at a load of 10 g (HV0.01) and statistically evaluated. Due to the lower load the absolute hardness numbers are higher compared to a load of 1000 g. The histogram (Figure 4) shows different hardness ranges for soft (95Pt-5Ir) and hard (95Pt-1.8Au-2.7In-0.5Ru and

![Fig. 3. Information obtained by thermodynamic calculations using Thermo-Calc® software and the noble metal alloys database (SNOB3); (a) Isopleth section of the Pt-Ru-Ga system at a constant content of 95% platinum; (b) Scheil calculation for two alloy compositions (solid lines). The dashed lines show the solidification under equilibrium conditions (very slow cooling).](https://doi.org/10.1595/205651319X15487786873383)
95Pt-2Ru-3Ga+ alloys. 95Pt-5Ir and 95Pt-1.8Au-2.7In-0.5Ru, which do not show precipitation hardening, show relatively narrow hardness distributions. Alloy 95Pt-2Ru-3Ga+ shows a very wide hardness distribution from 194–309 HV0.01 due to the segregation of Ga in the interdendritic regions. The upper value is within the hardness range of 280–318 HV0.01 that is achieved for a precipitation hardened 952Pt-48Ga alloy (22).

4.2 Correlation of Mechanical Properties and Microstructure

As described above, the additions of Ga or In increase hardness. The mechanical properties were found to be dependent on the chemical composition of the alloys as shown in Table I. The effect of Ga addition is shown for selected alloys in Figure 5. If Ru is partially replaced by Ga, it results in a moderate increase of the strength values (YS and UTS), both in the as-cast and HIP conditions. If the Ga content exceeds 1.5% the effect of precipitation hardening causes a non-linear increase of strength over Ga content. As shown above, only the interdendritic regions display sufficiently high Ga content to allow precipitation hardening and HIP does not affect the strength levels.

The ductility values ($\varepsilon_f$ and ROA) are much more sensitive to HIP. As strength levels increase with increasing Ga content, a reduction of the ductility values can be observed at the same time in the as-cast condition. For Ga contents up to 1.5%, this reduction can be compensated by HIP. This means that the reduction in ductility is a result of increasing micro-shrinkage porosity with increasing Ga content. This is not surprising as the segregation tendency significantly increases when Ga is added to the alloy (Figure 4). HIP closes micro-shrinkage pores and restores the ductility values of the alloys with 1.5% Ga to the values for the binary alloy 95Pt-5Ru. If more than 1.5% Ga is added, the ductility in the as-cast condition decreases further due to increasing micro-shrinkage porosity. HIP can restore ductility caused by micro-shrinkage; however, after HIP the ductility of alloys with 2.1% Ga does not achieve the ductility of the binary 95Pt-5Ru alloy. This indicates that precipitation hardening caused an effective reduction in ductility for the alloys with Ga content over 1.5%. Due to the similar chemistry of Pt-In alloys it is expected that these alloys show a similar behaviour. The actual In concentrations above which precipitation hardening occurs requires further experimental evidence.

The effect of the addition of Co to replace Ru in 95Pt-Ru alloy is shown in Figure 5(b). 0.2% proof stress and tensile strength are hardly affected by changes in the chemical composition. 95Pt-Co
shows only slightly higher UTS than 95Pt-Ru. This small difference is rather surprising as the atomic mismatch of Co to the Pt matrix is about three times higher than the mismatch of Ru to Pt. Furthermore, the number of alloying atoms is larger in the case of Co compared to Ru due to the lower atomic weight of Co. The small difference might be attributed to the larger grain size that is usually observed in 95Pt-Co (12).

As described above, HIP has no effect on the strength properties. The effect of HIP is only significant for the ductility values of 95Pt-Ru. The effect of Co addition to 95Pt-Ru has been discussed in detail elsewhere (24). According to that study small additions (1–2%) of Co significantly improved form filling and surface quality. This work also showed that micro-shrinkage could be avoided while small grain size was maintained. If such findings can be confirmed, HIP would still be beneficial in 95Pt-Ru-Co alloys, but less important compared to 95Pt-Ru. The reason for such changes was also described (23, 24) based on thermodynamic considerations. The addition of Co to Pt-5Ru lowers the equilibrium solidus and liquidus temperatures. Therefore, lower casting temperatures are 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 can be explained by the alloy thermodynamics, i.e. the heat release as a function of temperature during solidification.

5. Conclusion and Summary

Extensive testing of fifteen different Pt alloys was undertaken to determine mechanical properties and microstructure in the as-cast and HIP conditions. To the authors’ knowledge, this is the most comprehensive and publicly available study on Pt casting alloys to date. The main conclusions from this study are as follows:

- Based on the solid solution hardening provided by different alloying elements the alloys were categorised into the three groups of soft (<120 HV1), medium-hard (120–150 HV1) and hard alloys (>150 HV1). Soft alloys typically contain Ir, Cu, Pd-Co or Rh as alloying additions. Medium-hard alloys are obtained by alloying with Ru and 95Pt-Co 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 Pt.
- Hardness is directly correlated with UTS. UTS can be estimated by multiplying the hardness value by the factor of ca. 3.3. This is valid in the as-cast and HIP conditions and is a typical value for face centred cubic materials.
- HIP largely eliminates internal micro-shrinkage pores and thereby restores the ductility of Pt alloys to their full potential. This is reflected by a significant increase in ductility and especially ROA. The effectiveness of HIP on ductility depends on the level of micro-porosity. The few alloys with low micro-porosity in the as-cast condition (e.g. 90Pt-10Ir) show no increase while those with a higher level of micro-porosity strongly benefit from HIP.
- The effect of HIP on the strength values (YS and UTS) is less pronounced. For most of the alloys UTS is only slightly affected by HIP. 0.2% proof stress remains constant for most alloys. For some alloys it decreases by 15–20% without clear trends. This might be an effect of casting defects, such as larger pores.
- Increasing strength levels are usually offset by decreasing ductility; as UTS increases ductility and ROA decrease with a roughly linear correlation between UTS and ROA. Such decreases are much more pronounced in the as-cast condition compared to the HIP condition.
- Alloys containing Ga or In show pronounced segregation of these low melting elements to the interdendritic areas. This increases the amount of micro-shrinkage porosity and results in a greater inhomogeneity of the alloy’s composition and mechanical properties. HIP shows the most pronounced effect on ductility in alloys containing Ga or In. However, neither heat treatment nor HIP was sufficient to remove chemical inhomogeneities by diffusion.
- The addition of Ga or In results in precipitation hardening by Pt3Ga or Pt3In, respectively, if a critical level is exceeded. According to phase diagram information this level is about 2 mass%. However, due to the strong segregation of Ga and In, this critical level might be locally exceeded in the interdendritic regions. It is shown that even alloys with Ga or In contents of 1.5–2 mass% show local hardening of the interdendritic regions that can be explained by precipitation hardening. The actual In concentrations above which precipitation hardening occurs requires further experimental evidence.
- The partial replacement of Ru in 95Pt-Ru by Co significantly reduces shrinkage porosity while maintaining the small grain size that is beneficial for 95Pt-Ru. The properties of 95Pt-Ru-Co alloys in the as-cast condition hardly differ from those in the HIP condition.

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References


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