PLATINUM JEWELLERY CASTING ALLOYS: A COMPARATIVE STUDY OF SOLIDIFICATION BEHAVIOURS

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ABSTRACT

Platinum alloys are widely known to be quite challenging to cast, however the reasons for this are not well understood. Despite decades of experience, many casters continue to struggle with porosity, largely because a comprehensive data base of knowledge on platinum's solidification behaviours has not been available.

Through the use of controlled studies, we first explore the inherent solidification behaviours of several mainstream platinum casting alloys. In addition, we introduce hot isostatic pressing as an effective means to densify porosity in platinum alloy castings. Note: This is an edited and updated version of our 2011 paper "Platinum Alloys in the 21st Century: A Comparative Study" published in the Santa Fe Symposium Proceedings[i]

INTRODUCTION

Since its renaissance in the early 1990s, platinum jewellery has become a staple in bridal markets across the globe. Many consumers consider platinum to be the ultimate jewellery metal, in large part due it its rarity, purity, and long-term wear resistance when compared to gold alloys. Today, more than twenty-five years after its rebirth and well beyond manufacturers' initial learning curves, platinum remains one of most challenging jewellery metals to cast. Porosity and inclusions are commonplace, and even the best equipped casting operations have their fair share of rejections and costly rework. The reasons for this relate primarily to platinum's extreme high melting temperature combined with a limited understanding of its solidification behaviours in the various alloyed states.

This study aims to create a better understanding of the solidification behaviours of a number of commonly used platinum alloys. In doing so, we hope to aid manufacturers that are spending significantly more time finishing a platinum jewellery article than they would with high quality, and more specifically, high density castings.

PREVIOUS WORK

Awareness of the need for improved metallurgical performance in platinum alloys dates back to the mid-nineties when a wave of jewellery industry publications outlined concerns and possible solutions. The authors of these publications noted, among other things, that existing alloy compositions were too soft, too difficult to cast, too porous, and too time-consuming to polish.

One of the earliest of these publications was in 1995 when James Huckle of Johnson Matthey wrote one of the first comparative analyses of platinum casting alloys[ii]. Huckle's conclusions, which are summarized in Table 1, rate the mainstream alloys of the day in terms of relative quality.

Table 1 *Relative quality of castings*

Alloy Composition	**Large Rings (40g)**	**Engagement Rings (10g)**	**Fine Settings (< 1g)**
4.5 Ru-Pt	Very Poor	Poor	Poor
10 Ir-Pt	Good	Very Good	Satisfactory
4.5 Co-Pt	Very Good	Very Good	Very Good
15Pd-Pt	Very Good	Satisfactory	Satisfactory
4.5 Cu-Pt	Poor	Satisfactory	Poor

Source: James Huckle, 1995 Platinum Day Symposium

Huckle claimed that the Cu alloy was undesirable due to its tendency to form an oxide skin when molten, thereby reducing the fluidity of the alloy. Cu also formed an oxide layer on the as-cast surface and exhibited undesirable metal-to-mould reaction. The Ru alloy received low marks from Huckle, again due to metal-to-mould reaction, surface roughness, and the tendency toward no-fill. While Huckle gave a relatively favourable review to the casting quality of the Ir alloy, he ended up dismissing it for jewellery purposes due to its low mechanical properties. The Pd alloy was rejected due to excessive gas porosity and metal-to-mould reaction. Huckle's conclusion in terms of the best alloy for casting was the 4.5 Co-Pt, due to its good mechanical properties, lack of oxidation (other than a slight bluing of the surface), good fluidity, and the lack of any detrimental metal-to-mould reaction.

Three years later in 1998, renowned American jewellery designer and author Steven Kretchmer argued the need for a new platinum alloy[iii]. Kretchmer claimed that 95Pt5Ru and 90Pt10Ir were too soft and difficult to polish, and that porosity was frequently present due to excessive shrinkage on cooling and solidification. As a designer, Kretchmer argued from both a manufacturer's cost savings point of view as well as a consumer quality standpoint. He took a very comprehensive view of the effects that platinum alloy choices have on the entire downstream product cycle. Kretchmer's publication also contained information on a new and substantially harder alloy that was designed to address his concerns. He maintained that higher hardness improved polishing time by 25% when it fell into the 135-145 HV range. Kretchmer also highlighted his concern for soft alloys in terms of consumer satisfaction, stating that while consumers admired the beautiful neutral colour of platinum, they complained about the fact that the shine did not last and that dual tone finishes quickly burnished away.

In 1998, yet another publication by Todd, Busby, Landry, Linscomb and Gilman of Stuller, Inc., one of the largest jewellery manufacturers in the United States, asserted the need for a new casting alloy[iv]. They recognized that the then-current platinum casting alloys in use in North America were not designed specifically for investment casting, but rather for cold-forming applications that had been the historically used in platinum jewellery production prior to World War II. They were aware of the widespread use of 95Pt5Co for jewellery casting in Europe and decided to contrast this alloy with the prevailing alloys in use in the United States. Their research compared the casting quality for a number of metrics in 95Pt5Ru, 90Pt10Ir, and 95Pt5Co.

This pursuit by Todd et al. to identify an alloy that performed better than PtRu and PtIr led to their conclusion that 95Pt5Co was superior from raw casting through final polish, both in terms of polishing time and the presence of porosity. This research made 95Pt5Co the clear choice for their particular manufacturing and product applications, and as of this writing, Stuller continues to use this alloy predominantly in their casting operations.

Similar concerns were echoed in a 2000 publication "Platinum Alloy Design for Investment Casting" by Canadian metallurgist Greg Normandeau and co-author David Ueno[v]. In this paper, Normandeau and Ueno argued the need for an alloy that would fulfil a long list of desirable attributes when investment casting. These included form filling, recycle ability, resistance to formation of oxides or brittle compounds, colour, and enhanced wear performance. Normandeau and Ueno also noted that the issue of platinum durability was becoming a major concern for consumers who were disappointed when a soft alloy has been used for the designs they purchased. Like Kretchmer, an analysis of alloy performance beginning with casting and extending all the way through to the consumer experience was underscored. Normandeau and Ueno also emphasized the fact that a material with higher hardness will not only please the consumer with superior wear resistance, but also significantly reduce expensive hand polishing times for manufacturers.

In sum, it is clear that none of these authors was very satisfied with the casting quality of the leading platinum jewellery alloys cast in North America during the nineties. Notably, the dominance of these alloys remains the same today, with the exception that 95Pt5Co has gained a significant (although still minority) share of the market. Although there are certainly a greater number of alloys present on the global market today than in the mid-nineties, none has managed to solve all the problems that have historically challenged manufacturers and consumers. Even 95Pt5Co, widely held to be the best casting alloy in terms of solidification characteristics, continues to receive low marks from bench jewellers and retailers due to its oxidation, magnetic properties, and borderline hardness when compared to most karat golds.

In searching past literature, we also found a very limited amount of metallography visually demonstrating solidification patterns for platinum alloys. This was especially true for torus-shaped geometries that would demonstrate important dynamics for rings, the most common design used for platinum jewellery. The study by Todd et al. contained a small sampling of metallographic work on sprue sections for 95Pt5Co, 95Pt5Ru, and 90Pt10Ir, but nothing on cast jewellery geometries. Klotz and Drago published a larger number of metallographic sections for 95Pt5Co and 95Pt5Ru in the 2010[vi] and 2015[vii] Santa Fe Symposium® proceedings, but even with these additional efforts on solidification characteristics, a much more comprehensive understanding of different alloy compositions in a variety of geometries is needed for manufacturers that are challenged by porosity in their platinum castings. Jewellery designs are naturally becoming more complex with the dominant use of CAD for model creation, and a deeper understanding of what this means for the internal metallurgical quality of platinum castings is necessary to ensure high quality product.

EXPERIMENTAL METHODS

The metallographic study that follows is an important step in a direction closer to actual jewellery geometries, while still maintaining the tight control factors necessary to learn critical information about alloy solidification behaviours specific to different alloy compositions.

The casting experiments were carried out using centrifugal (horizontal swing-arm) casting machines with induction heating. The machines were equipped with optical pyrometers for temperature control and had options for vacuum or air melting. Two investments were used for the study, one being a ceramic shell system and the other a high-speed dental investment. A consistent flask temperature of 850°C (1562°F) was used as well as protective argon cover gas on all melts. Zirconium oxide-coated crucibles were used to ensure minimum interaction between the melt and the crucible material. Pouring temperatures were chosen between 1830° and 1900°C (3326° and 3452°F), depending upon the specific liquidus temperatures of the different alloys.

Solidification characteristics of 95Pt5Co, 95Pt5Ru, 90Pt10Ir, and a harder alloy labelled 950PtCo+ were evaluated. A test geometry specifically designed to encourage directional solidification was used. The graduating thicknesses are shown in Figure 2a and b, as well as the locations for the sprue attachments. The tie-bar, not originally included in the design, had to be added for stability during sectioning with a jeweller's saw.

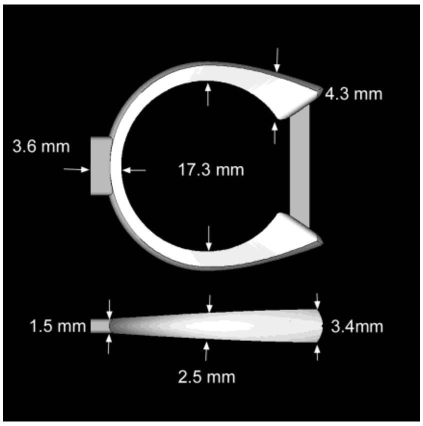

Figure 2a *Single Bottom Sprue*

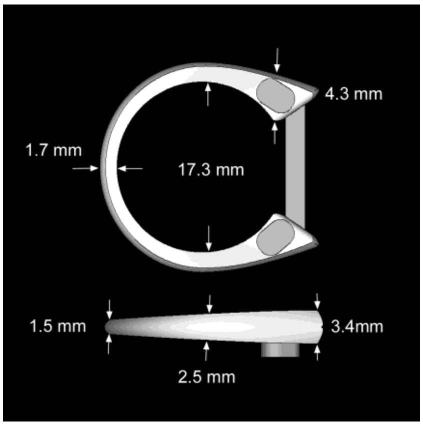

Figure 2b *Double Top Sprue*

The casting parameters for our trials are shown in Table 3. These were selected with the aim of demonstrating the differences in solidification that occur through the use of different sprue systems, casting atmospheres, and investments. With respect to spruing, the single sprue, which we anticipated would constrict flow of the molten feed to the casting, was chosen to graphically demonstrate the danger of using such a system. The double sprue approach, considered optimal in a directionally solidified geometry, aims to depict a best-case scenario for solidification in each particular alloy.

Table 3 *Casting parameters*

Alloy	**Sample Type**	**Gating**	**Flask °C/°F**	**Pour °C/°F**	**Atmosphere**	**Investment**
Set A						
95Pt5Co	Shank	Single Bottom	850/1562	1850/3362	argon only	shell
95Pt5Ru	Shank	Single Bottom	850/1562	1900/3452	argon only	shell
90Pt10Ir	Shank	Single Bottom	850/1562	1900/3452	argon only	shell
95PtCo+	Shank	Single Bottom	850/1562	1830/3326	argon only	shell

Set B						
95Pt5Co	Shank	Double Top	850/1562	1850/3362	argon only	shell
95Pt5Ru	Shank	Double Top	850/1562	1900/3452	argon only	shell
90Pt10Ir	Shank	Double Top	850/1562	1900/3452	argon only	shell
95PtCo+	Shank	Double Top	850/1562	1830/3326	argon only	shell
Set C						
95Pt5Co	Shank	Double Top	850/1562	1740/3164	vac / argon	shell
95Pt5Ru	Shank	Double Top	850/1562	1800/3272	vac / argon	shell
90Pt10Ir	Shank	Double Top	850/1562	1800/3272	vac / argon	shell
95PtCo+	Shank	Double Top	850/1562	1700/3092	vac / argon	shell
Set D						
95Pt5Co	Shank	Double Top	850/1562	1850/3362	argon only	high-speed dental
95Pt5Ru	Shank	Double Top	850/1562	1900/3452	argon only	high-speed dental
90Pt10Ir	Shank	Double Top	850/1562	1900/3452	argon only	high-speed dental
95PtCo+	Shank	Double Top	850/1562	1830/3326	argon only	high-speed dental

** The vacuum/argon category trials were carried out on a machine that allowed for the required variation in melting atmosphere. Due to the crucible size and distance from the induction coil, temperatures could not be raised to the same level as for other trials. The optical pyrometer read a significantly lower pouring temperature between ~ 1700 and 1800 °C, although real temperatures were most likely only slightly higher than the actual melting temperatures for each alloy.*

RESULTS

A first overview of the results (shown in detail in Figures 3-6) suggests that independent from specific casting parameters, 95Pt5Co performs the best from a shrinkage porosity standpoint and 95Pt5Ru performs the worst. The 90Pt10Ir is very close to 95Pt5Co, and the hard 95PtCo+ alloy is slightly inferior to 95Pt5Co with small but consistently higher levels of micro-porosity.

Fluidity of alloys is most often referred to as beneficial for form filling. While this is certainly true, the higher fluidity of an alloy is also critical for feeding during the solidification process in order to minimize the formation of shrinkage porosity. The superior fluidity seen in the form filling properties of 950 PtCo in comparison to 950 PtRu and other alloys would suggest better feeding properties for 950 PtCo during solidification. As seen in all 950 PtCo casting conditions, porosity is significantly lower than the other alloys.

The comparison of results from set A (single bottom sprue system) and set B (double top sprue system) clearly demonstrate that comparably thick and multiple sprues attached to heavy sections of the pattern are mandatory for obtaining acceptably low levels of porosity in all of the tested alloys. With the single bottom sprue system, all alloys apart from 95Pt5Co develop huge cavities in the thick upper areas of the geometry (Figures 3a-d). Both shrinkage and gas porosity accumulate in areas that solidify last. A tremendous reduction in porosity is obtained for all alloys if a well-designed sprue system is used (Figures 4a-d). 95Pt5Ru develops a comparably large amount of scattered shrinkage porosity regardless of sprue system. The results from set C, a double top sprue system in combination with an oxygen-free melting atmosphere, do not yield uniform and conclusive results for all alloys. While a significant reduction in porosity is observed for 95Pt5Ru (Figure 5b), the corresponding improvement for 95PtCo+ is low (Figure 5d) and the opposite is observed for 90Pt10Ir (Figure 5c). For 95Pt5Co the porosity is lowered in most areas, but two huge gas pores pop up on the ring shank (Figure 5a).

In contrast to this, the fact that gas porosity still occurs in significant amounts for 95Pt5Co and 90Pt10Ir, even in an oxygen-free melting atmosphere, does not support the view that uptake of oxygen by the melt is an issue for platinum casting, at least for those alloys. Instead the results of set D, double top sprue system in combination with “high-speed” dental investment, suggest that the conditions for escape of gas (air or argon) through the mould material play an important role (Figures 6a-d). Overall a lower amount of gas porosity is observed for all alloys, especially for 95Pt5Co and 90Pt10Ir in the samples for set D. It is assumed dental investment has higher gas permeability than shell mould material, which would explain an overall lower presence of trapped gas bubbles in the castings of set D. While gas was apparently affected, the typical characteristics between the alloys in terms of amount and distribution of shrinkage porosity were the same for either a shell mould system or the high-speed dental investment.

Lastly, it should also be acknowledged that the potentially lower and less reliable reading on the pour temperatures for the samples of Set C (see Table 3 sub-text) may have contributed to the apparent inconsistency in these particular results. It is possible a combination of poor melting atmosphere and excessive time at a molten state in the crucible may have contributed to some of the higher porosity levels seen.

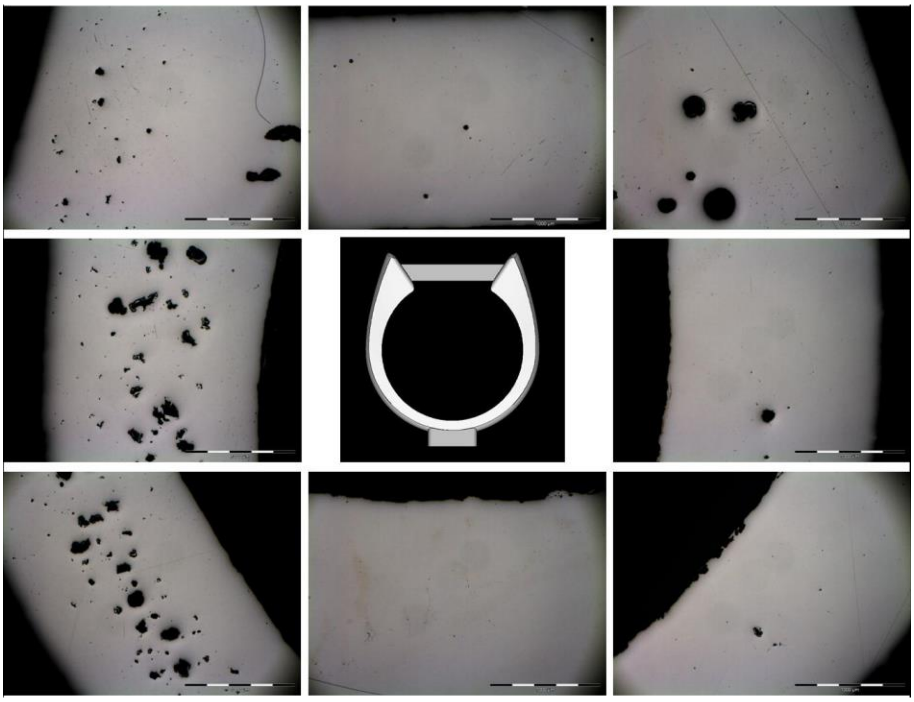

Figure 3a *95Pt5Co, Set A, single bottom sprue*

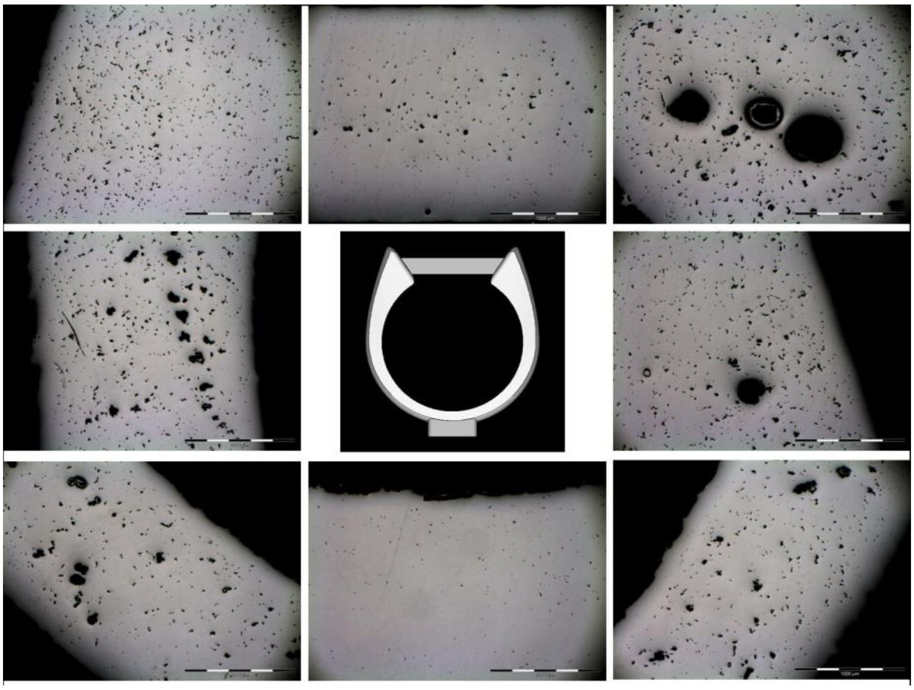

Figure 3b *95Pt5Ru, Set A, single bottom sprue*

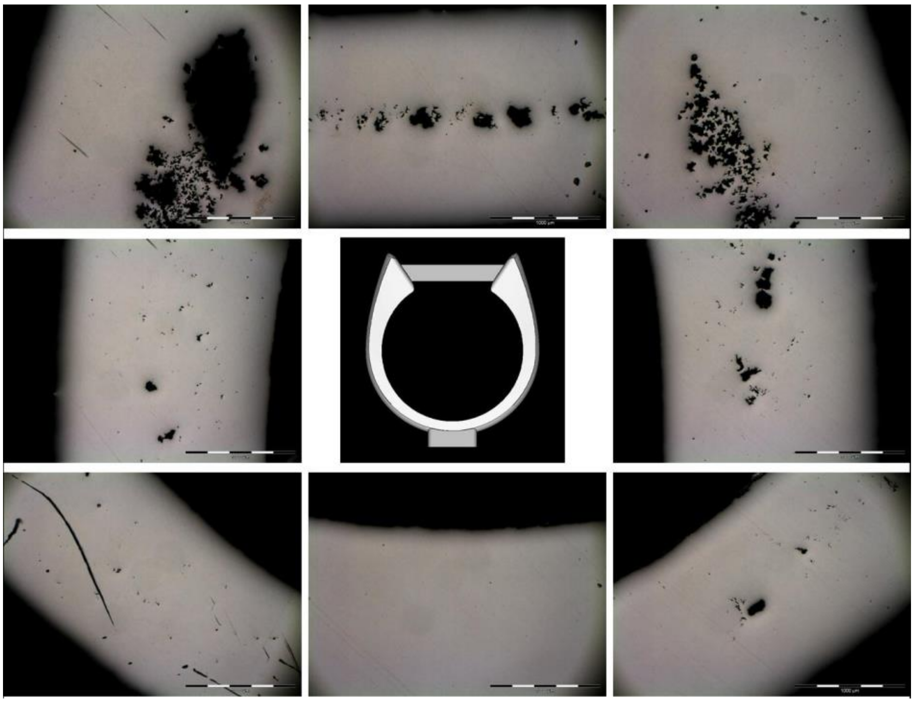

Figure 3c *90Pt10Ir, Set A, single bottom sprue*

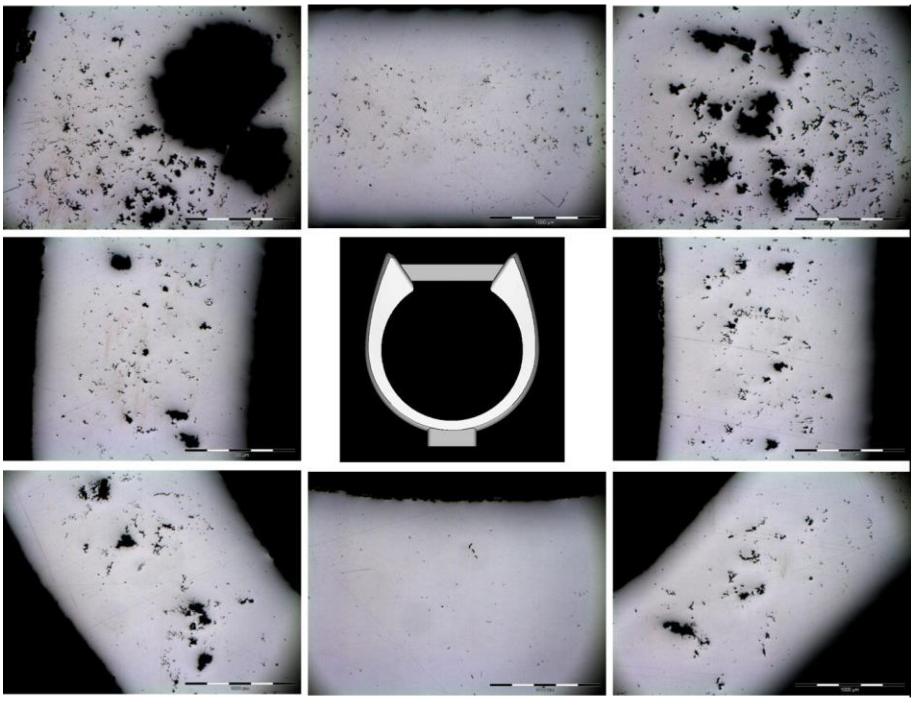

Figure 3d *95PtCo+, Set A, single bottom sprue*

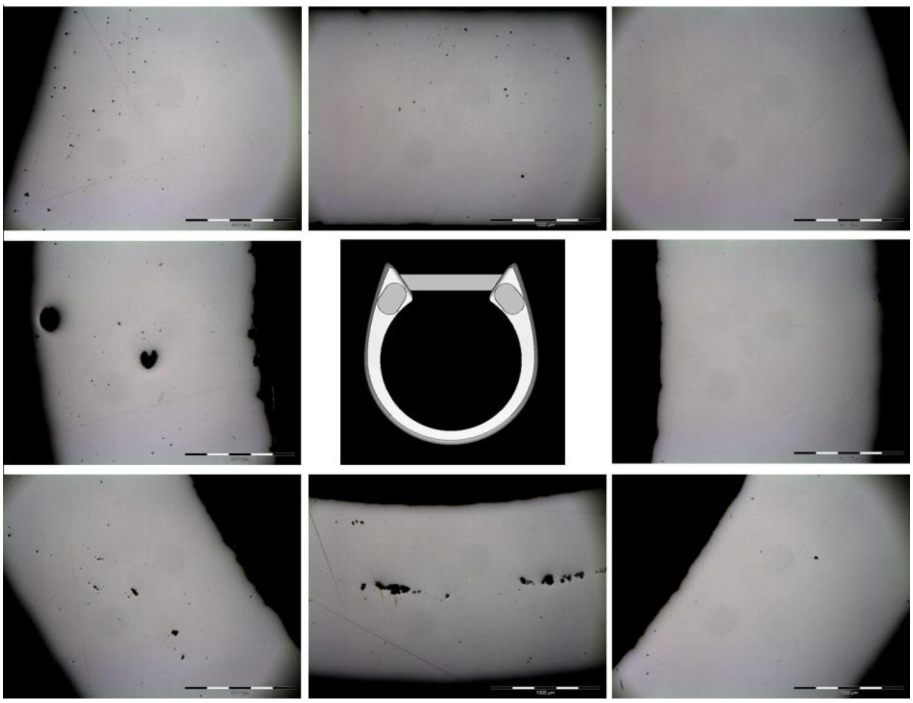

Figure 4a *95Pt5Co, Set B, double top sprue*

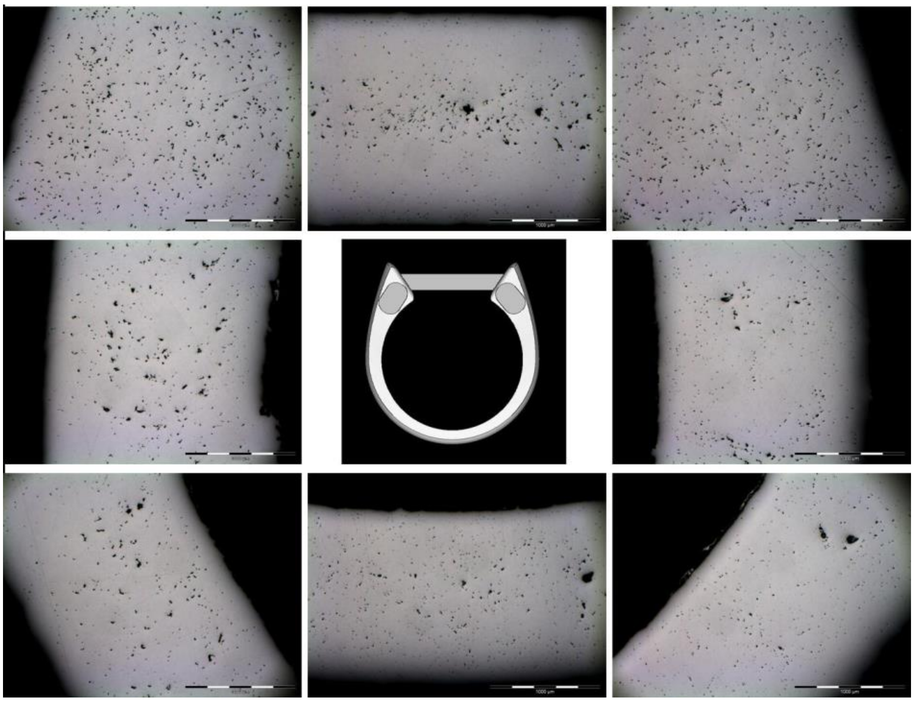

Figure 4b *95Pt5Ru, Set B, double top sprue*

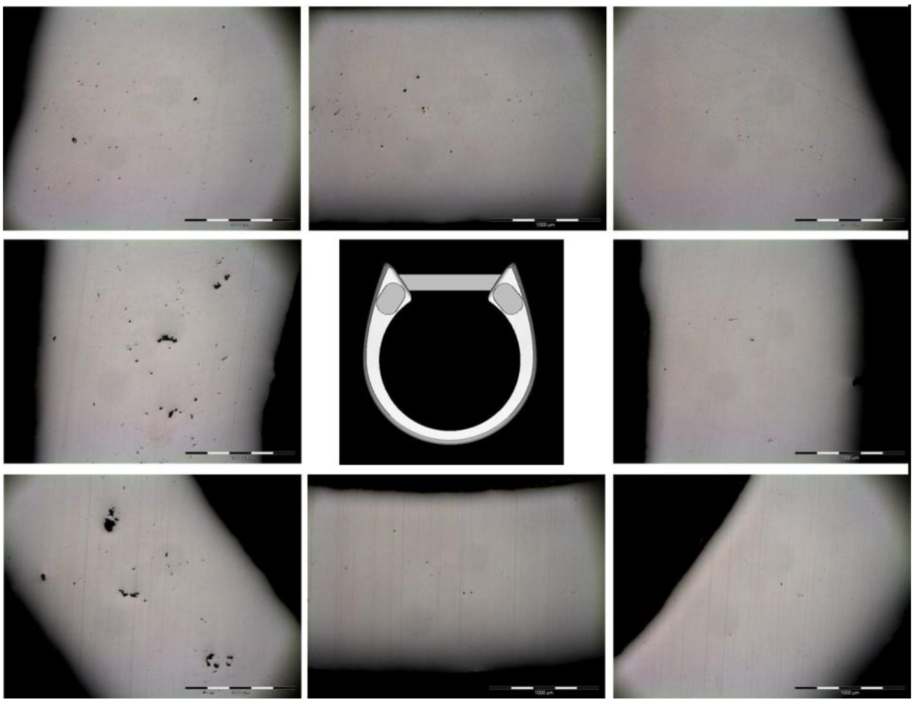

Figure 4c *90Pt10Ir, Set B, double top sprue*

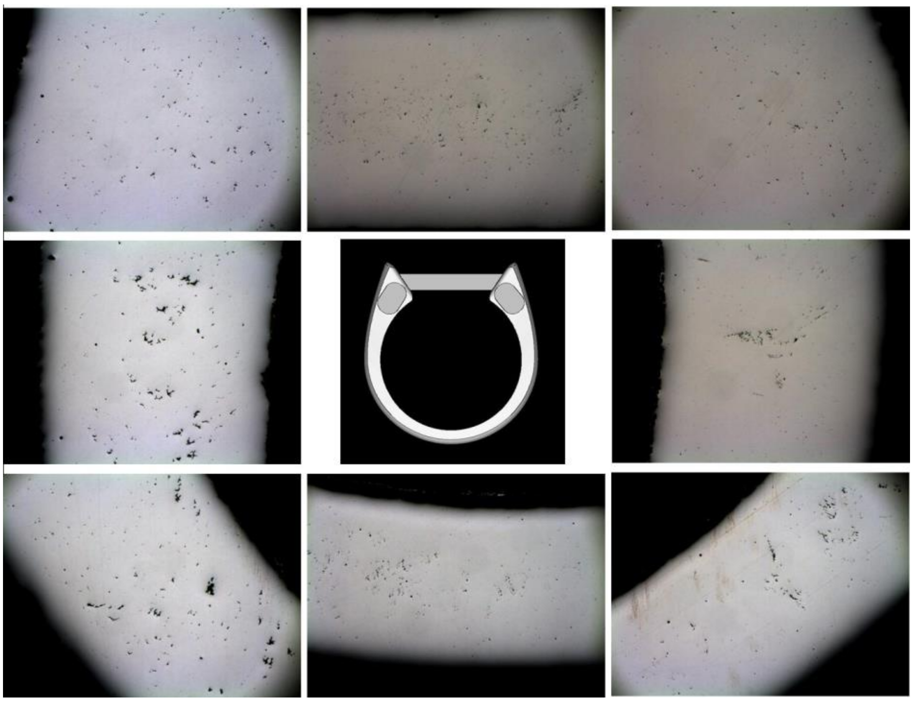

***Figure 4d** 95PtCo+, Set B, double top sprue*

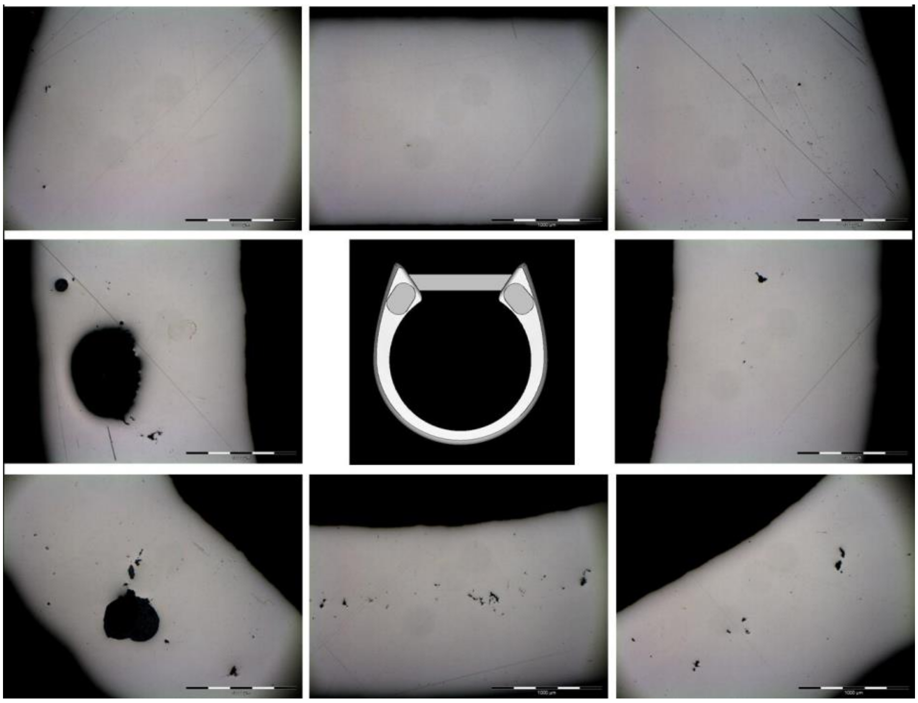

***Figure5a** 95Pt5Co, Set C, vacuum/argon*

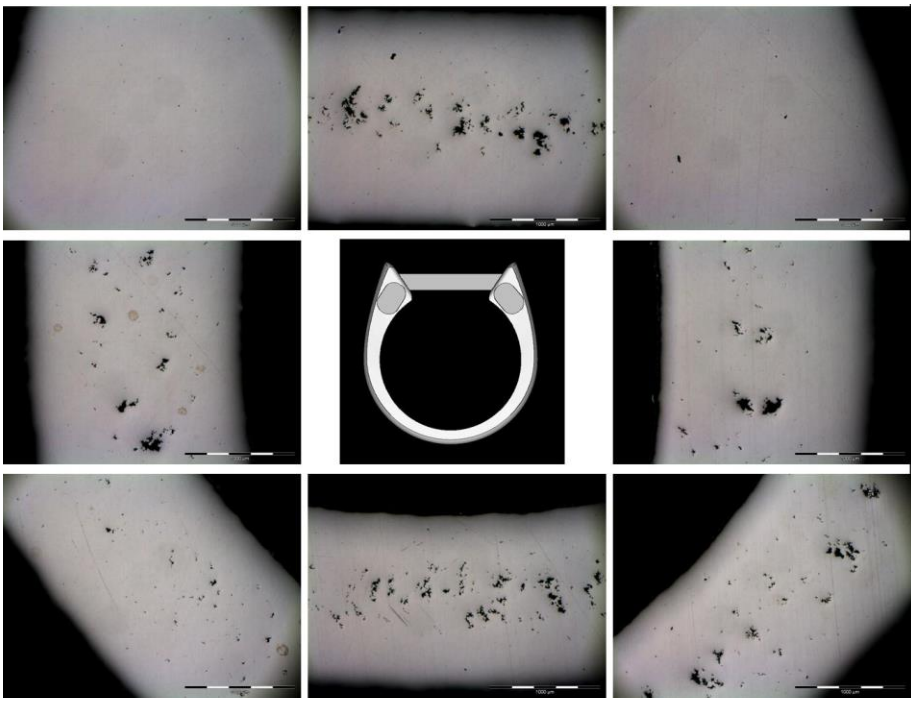

***Figure5b** 95Pt5Ru, Set C, vacuum/argon*

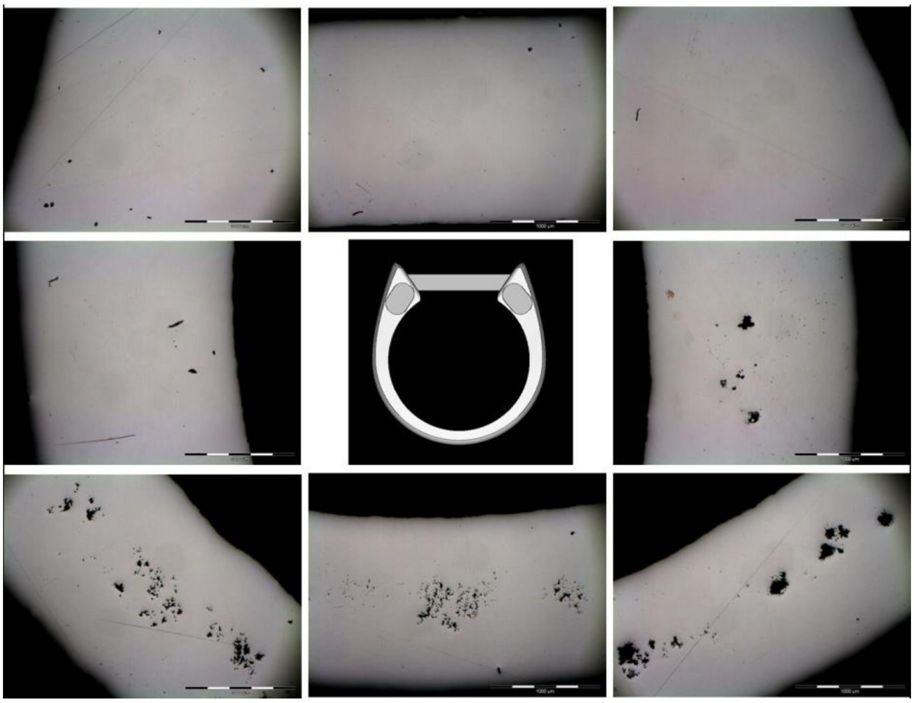

***Figure 5c** 90Pt10Ir, Set C, vacuum/argon*

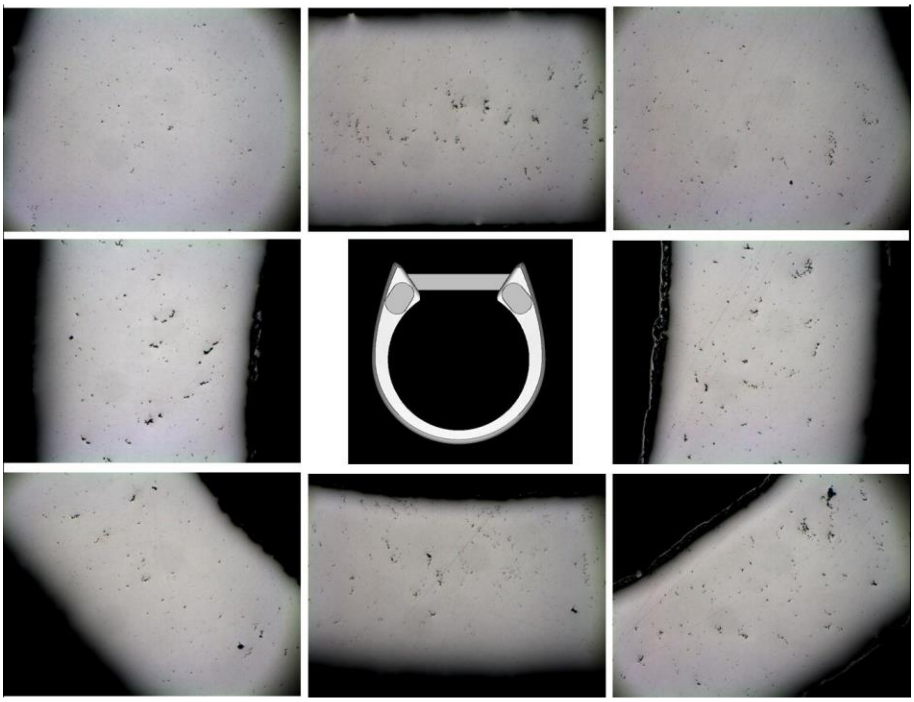

Figure 5d *95PtCo+, Set C, vacuum/argon*

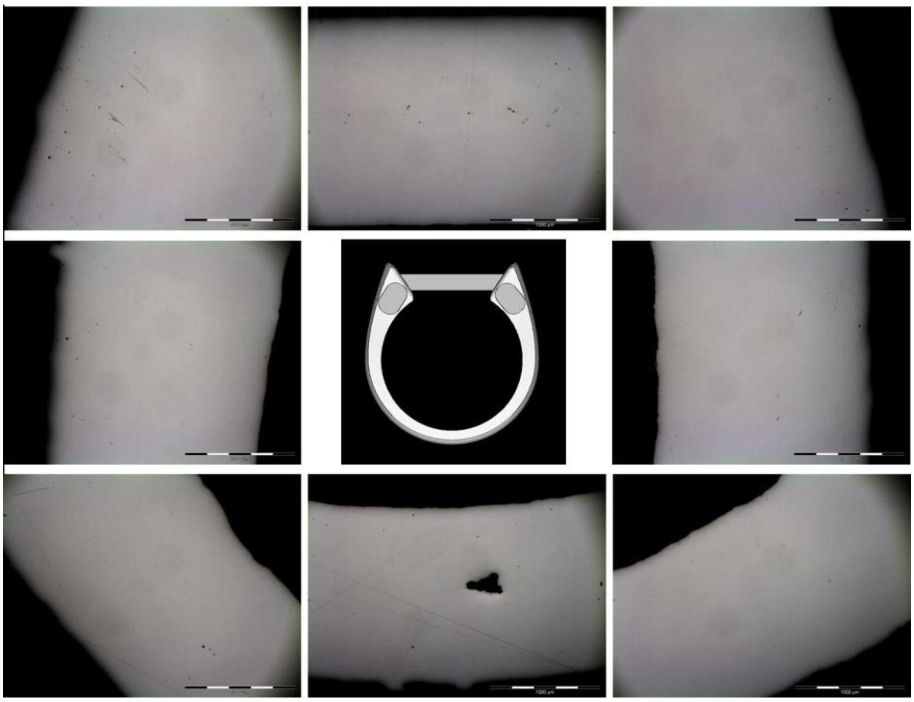

Figure 6a *95Pt5Co, Set D, high-speed dental investment*

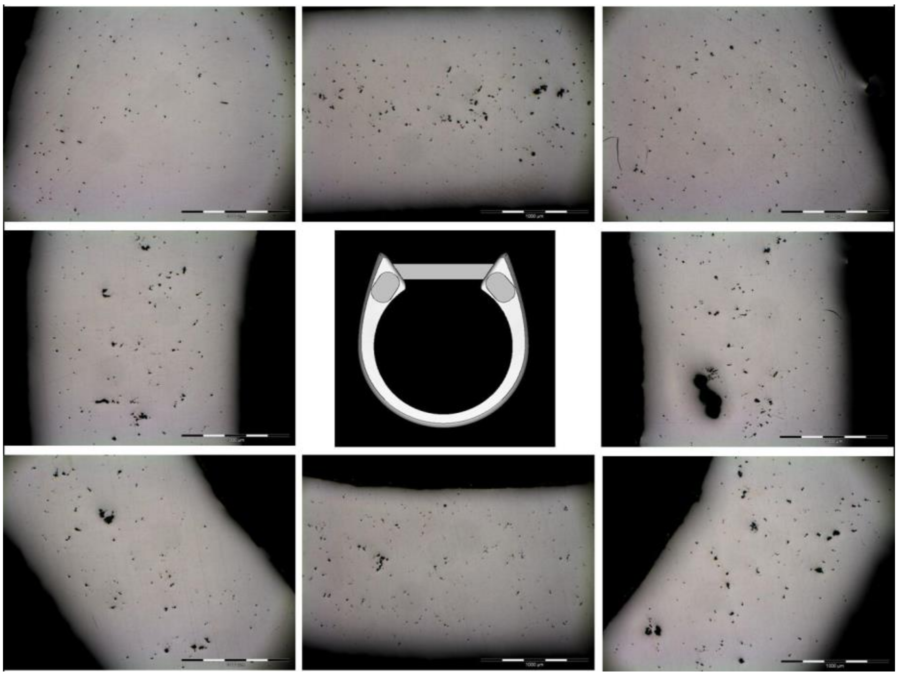

Figure 6b *95Pt5Ru, Set D, high-speed dental investment*

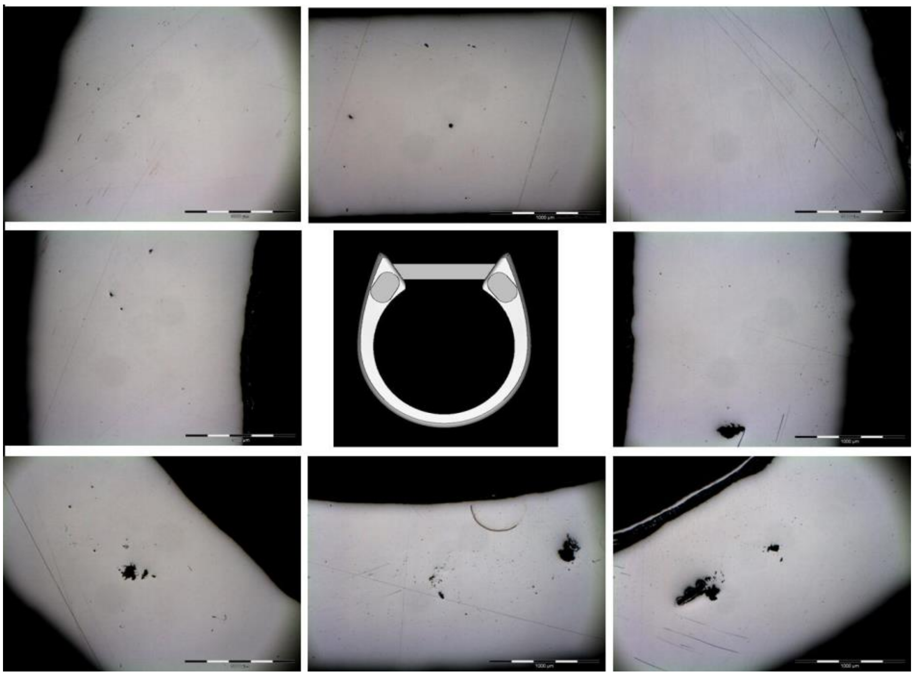

Figure 6c *95Pt10Ir, Set D, high-speed dental investment*

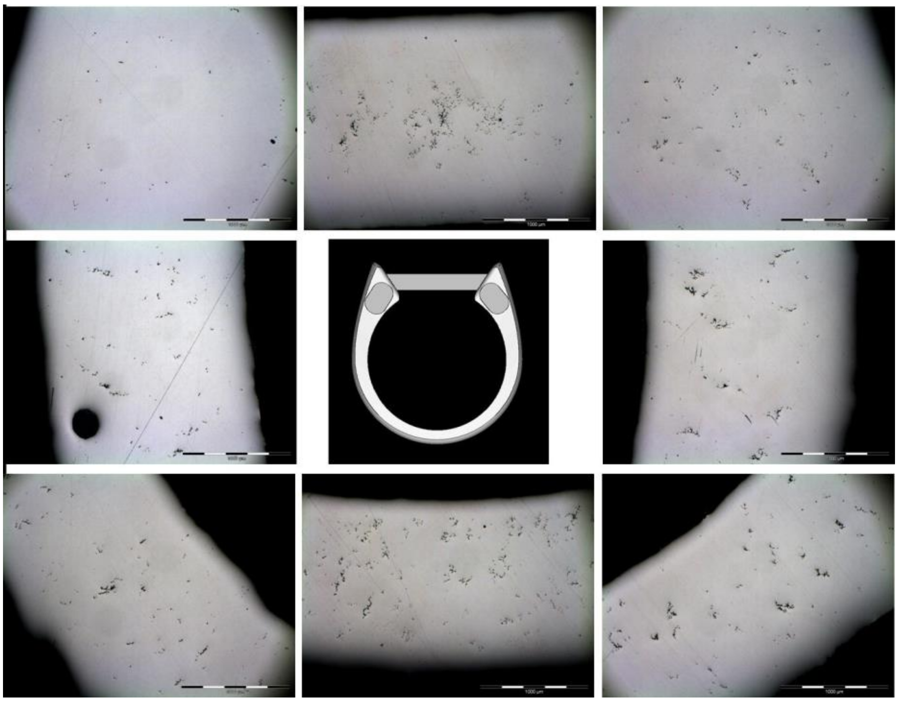

***Figure 6d** 95PtCo+, Set D, high-speed dental investment*

FURTHER PROPERTIES OF THE HARD 950PT5CO+ ALLOY

The detailed metallographic analysis raises some hope that porosity levels nearly as low as those for 95Pt5Co can be consistently obtained in a significantly harder alloy based on a 95Pt5Co+ composition. An increase of as-cast hardness from ~135 HV for the standard 95Pt5Co alloy to ~ 175 HV for the 95Pt5Co+ is obtained by replacing approximately 1wt% of Co with In. Many of the harder ternary platinum alloys have shown a greater tendency towards uniform and scattered shrinkage porosity close to the polishing surface, while the 95PtCo+ exhibits a smaller amount that also moves toward the centre line and remains further away from the polishing surface. As discussed in our earlier publication on this subject[viii], it is assumed that the comparably low level (~ 1 wt.%) of alloying additions that is required to increase the hardness of 95Pt5Co is essential.

Another very interesting and highly beneficial aspect of this alloy is that with ~1% alloying addition the 95PtCo+ loses its ferromagnetic properties. In the past, magnetism has contributed significantly to the low acceptance of 95Pt5Co alloys, especially in North America. For bench operations involving heat, platinum that has magnetic properties carries with it the risk of contamination from iron that might accidentally bond to the jewellery article. This attribute alone is a very significant benefit in a PtCo-based alloy.

With regard to further casting properties, additional results suggest that the alloying additions slightly alter the viscosity and fluidity of 95Pt5Co so that moderately higher (+20-30°C/+36-54°F) pouring temperatures are required for the hard 95PtCo+ to obtain similarly good form filling results as for the standard 95Pt5Co alloy. Both Co-containing alloys easily fill a test grid pattern at the standard pouring conditions used in this study, while 95Pt5Ru and 90Pt10Ir fail to achieve complete fill (Figure 7).

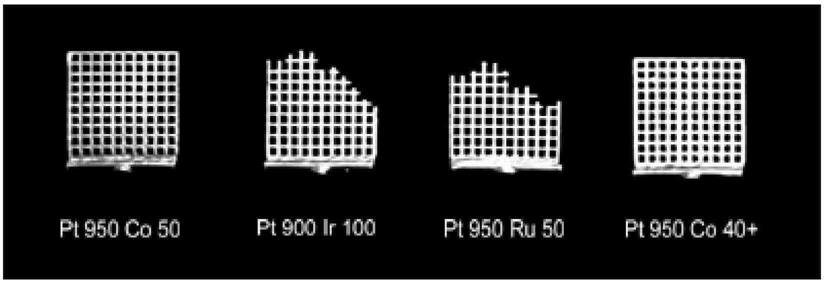

Figure 7 *Grid fill tests*

Finally, the etched microstructures shown in Figures 9a & 9b document that a smaller as-cast grain size is obtained for 95PtCo+ when compared to 95Pt5Co. The solidification microstructure changes from comparably large and columnar grains in 95Pt5Co to predominantly equiaxed, finer grains in 95PtCo+. The etched microstructures illustrate that the growth of columnar grains yields to the typical accumulation of centre-line porosity in the case of 95Pt5Co, while a more scattered distribution of micro porosity is associated with the equiaxed solidification microstructure of 95PtCo+.

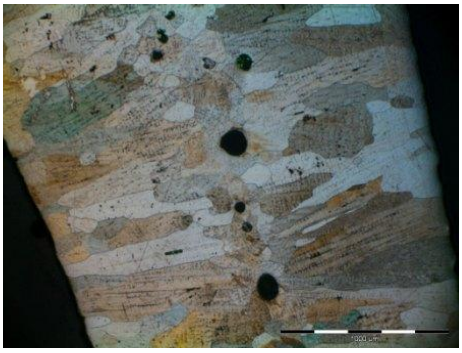

Fig9a *Grain structure 95Pt5Co*

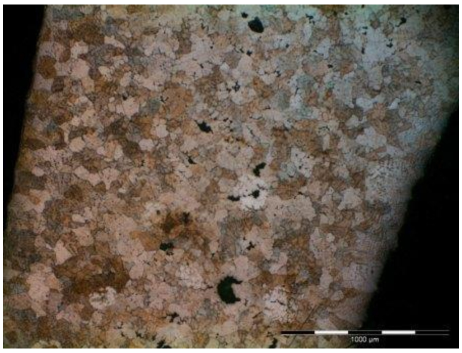

Fig9b *Grain structure 95PtCo+*

COMPARATIVE TRADE SAMPLING

In seeking confirmation of the solidification characteristics identified in our experiments, we thought it would be useful to do a small blind sampling of castings produced at platinum trade casters in North America. We selected three different alloys–95Pt5Ru, 95Pt5Co, and 95PtRu+, one of the hard platinum alloys. The same test patterns from Part II of the study were used to provide a good match for solidification comparison. No spruing instructions were given, leaving it up to individual casters to best sprue for the design. The resulting cross sections exhibiting the solidification patterns of these castings are shown in Figures 10a-c.

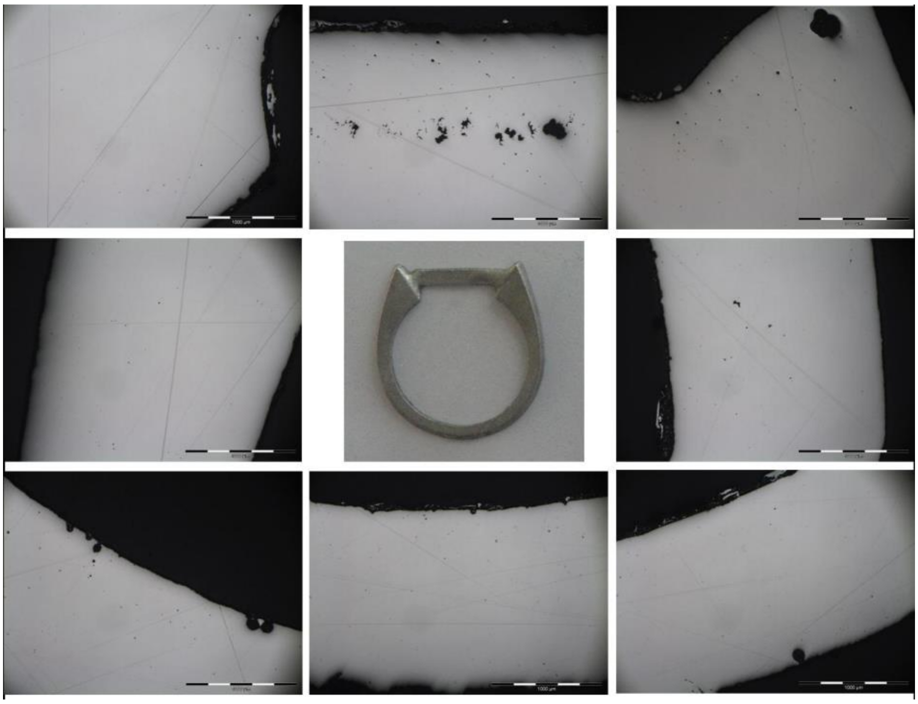

Figure 10a *Trade casting 95Pt5Co*

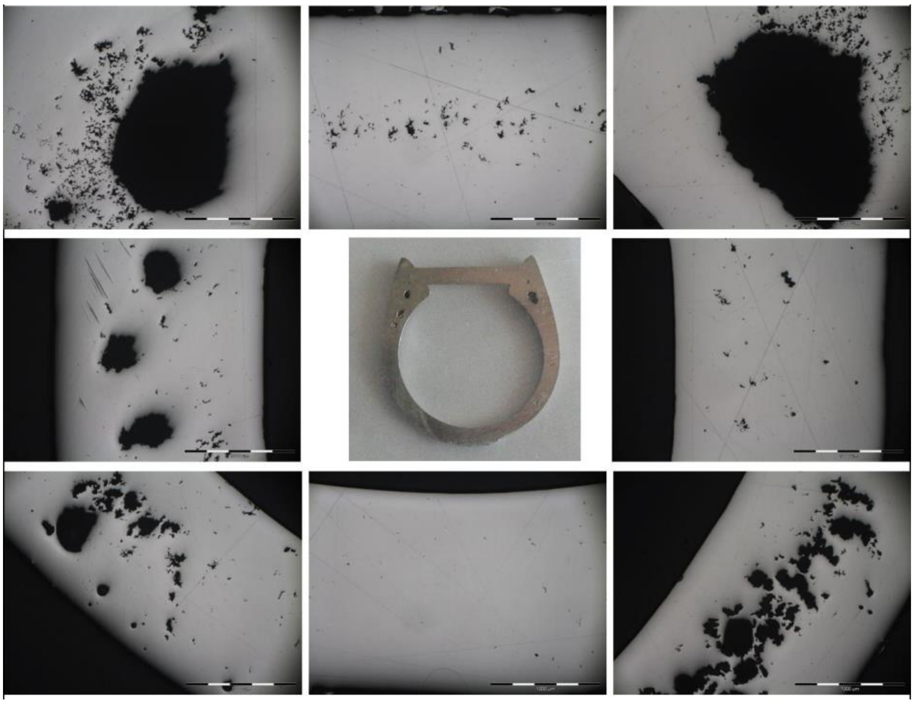

Figure 10b *Trade casting 95Pt5Ru*

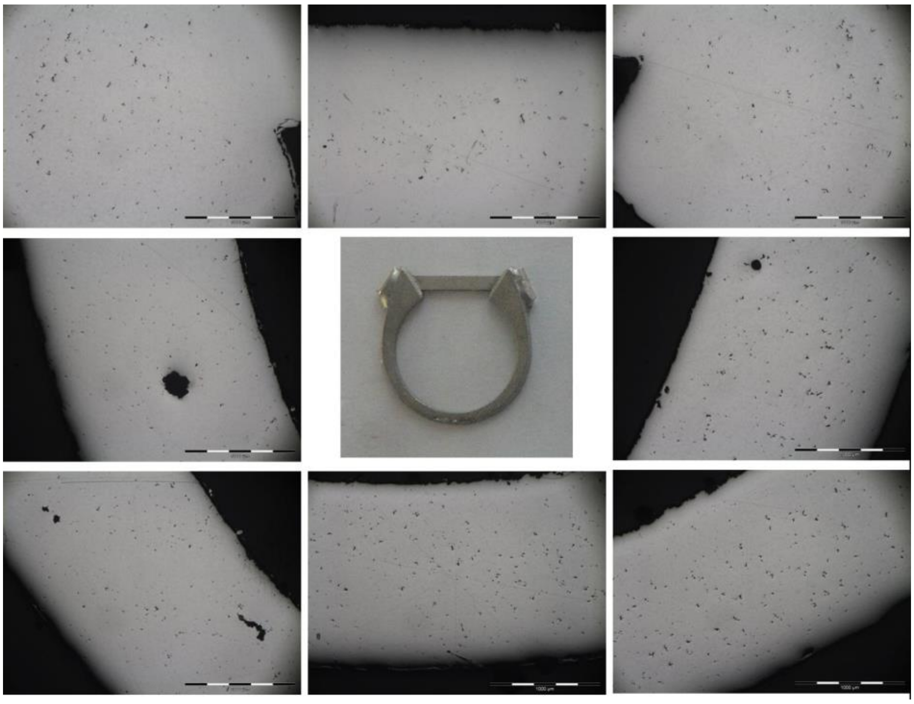

Figure 10c *Trade casting 95Pt5Ru+*

As we can see, the results for the 95Pt5Ru are catastrophic. This caster chose to use a single bottom sprue, an approach that severely restricted the molten metal feed to the casting. This led to tremendous porosity all over the sample, which accumulated in the thick shoulder areas (Figure 10b). In contrast, a much better sprue system was used by the casters of the 95Pt5Co and 95PtRu + alloys. For 95Pt5Co no shrinkage porosity but some spherical gas pores are observed that accumulate in the centre-line region as well as areas near the surface (Figure 10a). In the 95PtRu + casting, scattered shrinkage micro-porosity is observed in a fairly uniform manner over the entire sample together with a few larger cavities (Figure 10c). Apart from the sprue system, no details about casting parameters and mould materials used by the different casters were available to us, so differences between the alloys cannot be discussed on a scientific basis. In agreement with our own results, this study brings further confirmation that independent of the sprue system and the investment, the alloy's composition can have a significant influence on the amount and distribution of porosity and as-cast quality.

HOT ISOSTATIC PRESSING

Given the extreme difficulty of casting platinum alloys that are free of shrinkage porosity, we launched a final experiment to see what effect hot isostatic pressing would have on the macro and micro structures of our platinum alloy castings. HIP is a high-pressure thermal treatment that is routinely used on investment castings in numerous industries where high-density castings are often mandated by a particular material specification. The HIP process involves placing the castings into a high-pressure vessel for a specified period of time with inert gas applying the pressure at elevated temperatures. The result is densification, which happens when the material's creep resistance is surpassed and plastic flow enables the surrounding material to move into voids. Time at temperature allows diffusional bonding to occur, which eliminates any internal porosity. For further information on HIP of platinum alloys, a detailed study of its effects on the mechanical properties and microstructures of platinum alloy castings was published in 2014 by Frye et al.[ix] For our HIP experiments the entire casting tree was sent out for processing because the HIP process will only heal porosity that is not exposed in any way to the surface of the casting. Leaving the castings on the tree safeguarded that any porosity under the sprues would likely be HIPed out of the casting. The casting parameters used for the HIP samples were the same as set B in Figure 4. Below are the metallographic sections following the HIP cycle (Figure 11).

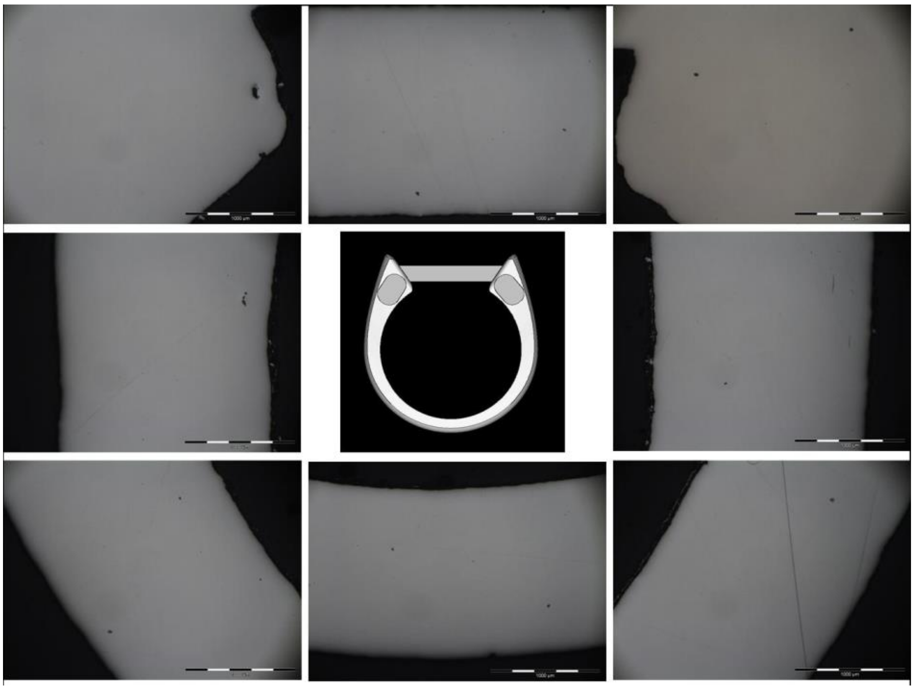

Figure 11a *HIP-treated 95Pt5Co*

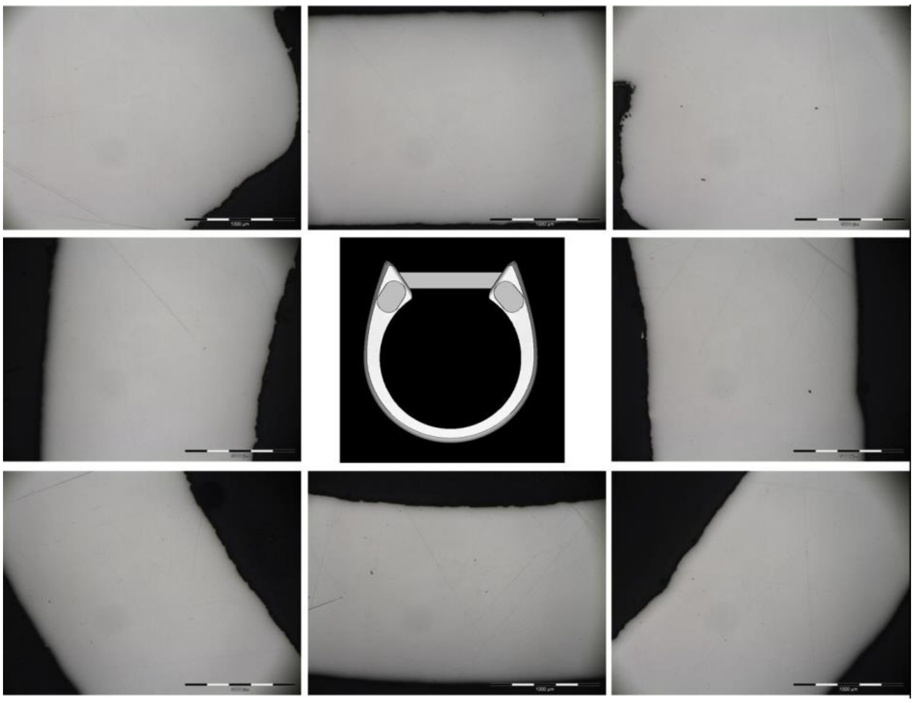

Figure 11b *HIP-treated 95Pt5Ru*

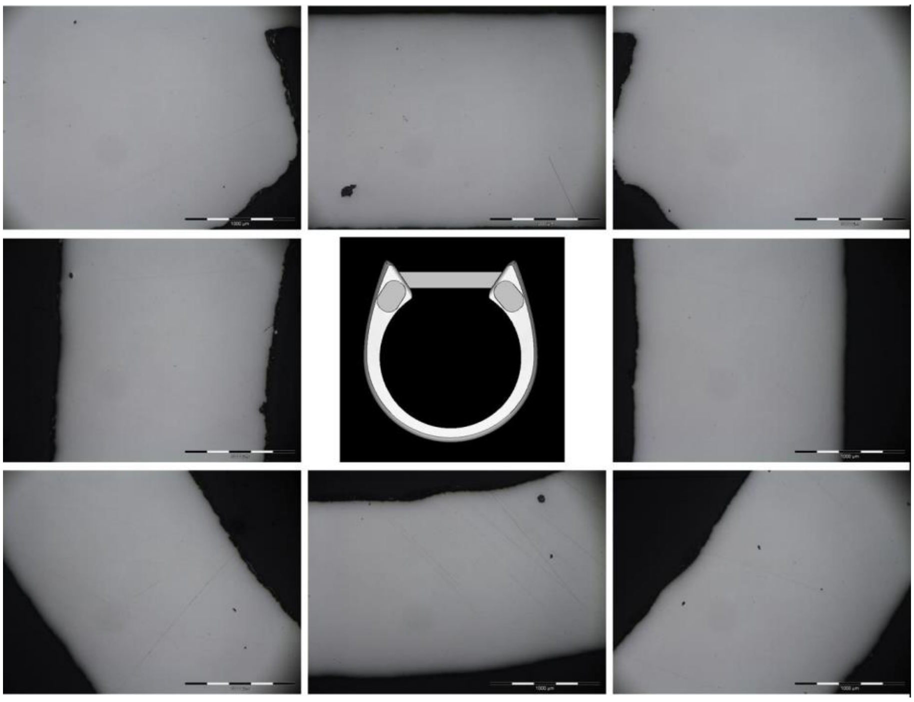

Figure 11c *HIP-treated 90Pt10Ir*

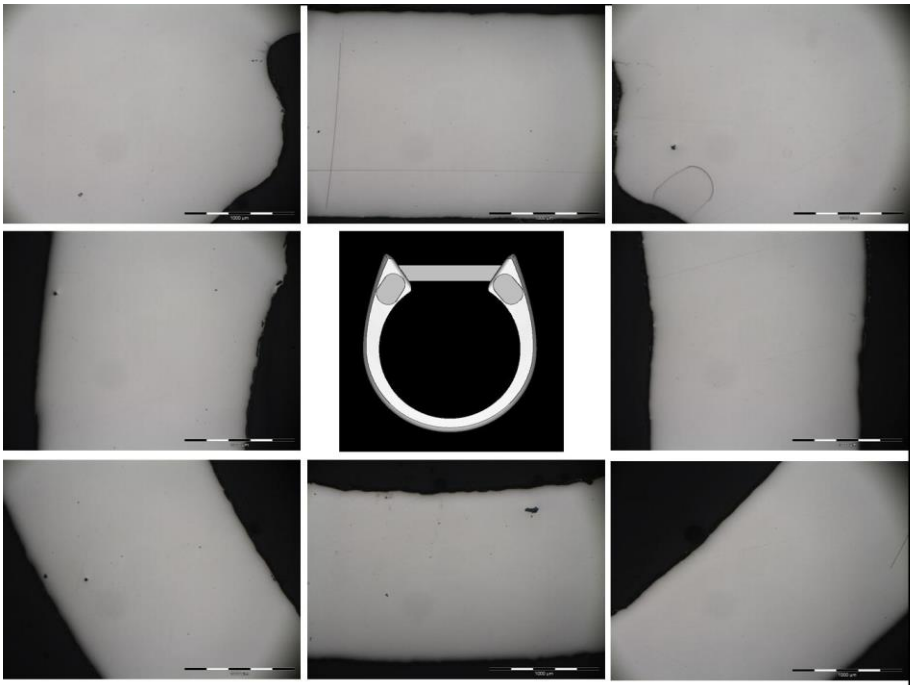

Figure 11d *HIP-treated 95PtCo+*

Almost no porosity is left after the HIP treatment for all castings. Any micro-porosity was completely closed, while the few smaller cavities that are still present are likely the remainders of some larger gas pores that contained pressure and thus were not able to completely close during the HIP treatment.

CONCLUSIONS

Platinum jewellery manufacturing operations are strongly impacted by the characteristics of the particular alloy they choose to use. Beginning with casting and continuing all the way through to the consumer experience, alloy choice has significant cost and quality implications. Solidification behaviours and their effects on porosity levels directly impact the polishing labour required to finish a jewellery article. This and other characteristics such as ability to fill fine sections all affect scrap and rework costs in production settings.

In summary, the detailed metallographic work that has been done in this research confirms many of the claims made in the earlier trade publications mentioned at the beginning of this paper. Specifically, additional data demonstrates that 95Pt5Co exhibits not only superior form filling, but also much lower shrinkage porosity in comparison with 95Pt5Ru.This data is useful towards seeing the impact of increased fluidity in platinum alloys.

It is our hope that through this study we have demonstrated that a number of technical solutions exist toward improving the quality of platinum jewellery castings. Whether a solution through the improved solidification characteristics of the PtCo-based alloys or the use of hot isostatic pressing to densify shrinkage-prone alloys, opportunities for improvement were highlighted through this research.

ACKNOWLEDGEMENTS

The authors would like to extend a special thanks to Riccardo Bertoncello and his colleagues from the Legor R&D Lab who meticulously prepared the numerous metallographic sections for our research; and Massimo Poliero, managing director at Legor, for having supported this project. Thanks also to the team at TechForm Advanced Casting Technology for carrying out our casting experiments with such diligence, to Steven Adler of A3DM for CAD/CAM support, and to Joseph Strauss at HJE Co for HIP advice. We would especially like to acknowledge the good work of the many authors who preceded us on this subject, and whose observations and solutions to the issues surrounding the casting of platinum alloys provided a solid foundation for our research.

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