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Nearly 20 years after its renaissance as a popular jewelry metal, platinum remains one of the most difficult materials to cast. Even the most sophisticated and experienced casting operations face challenges in attaining consistently dense castings. This original research takes a close look at the solidification behaviors of several mainstream platinum alloys as well as high pressure thermal treatment of castings to increase density.

Platinum Alloys in the 21st Century: A Comparative Study

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Introduction

Since its renaissance in the early nineties, platinum jewelry has become a staple in bridal markets across the globe. Many consumers consider platinum to be the ultimate jewelry metal, in large part due to its rarity, purity, and longevity when compared to gold alloys. Today, more than fifteen years after its rebirth and well into manufacturers' learning curves, platinum remains one of the most difficult jewelry metals to cast. Porosity and inclusions are commonplace, and even the best-equipped casting operations will have their fair share of rejections and costly rework. The reasons for this are often attributed to platinum's high melting temperature and density, combined with a limited understanding of its solidification behaviors in the various alloyed states.

In addition to manufacturers' challenges, both consumers and retailers express disappointment in the visual wear resistance of some platinum jewelry. In North America, consumers tend to wear their bridal jewelry on a daily basis and the majority of them prefer a high luster finish. Many of the softer platinum alloys are subject to excessive denting, scratching, and loss of high luster after everyday wear.

This study has a two-fold aim towards addressing these concerns. First, we hope to better understand the solidification behaviors of a number of platinum alloys that are used in the North American jewelry industry today. This will address the concerns of manufacturers that spend significantly more time finishing a platinum jewelry article because they encounter excessive porosity. Second, we will attempt to define which alloys should perform best from a consumer satisfaction point of view, particularly with respect to hardness. Metallurgical results will be reported for 950 PtRu, 950 PtCo, 900PtIr, and several Pt950 alloys containing elements that substantially increase hardness. Characteristics to be assessed include shrinkage porosity, form filling, hardness, and the effects of thermal post-processing of castings.

Previous Work

Awareness of the need for improved metallurgical performance in platinum alloys dates back to the mid-nineties when a wave of jewelry 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 alloys¹. Huckle's conclusions, which are summarized in the table below, 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 mold reaction. The Ru alloy received low marks from Huckle, again due to metal to mold reaction, surface roughness, and the tendency toward no-fill. While Huckle gave a relatively favorable review to the casting quality of the Ir alloy, he ended up dismissing it for jewelry purposes due to its low mechanical properties. The Pd alloy was rejected due to excessive gas porosity and metal to mold reaction. Huckle's conclusion in terms of the best alloy for castings 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 mold reaction.

Three years later in 1998, author and renowned American jewelry designer Steven Kretchmer argued the need for a new platinum alloyⁱⁱ. Kretchmer claimed that 950 PtRu and 900 PtIr were 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 Vickers range. Kretchmer also highlighted his concern for soft alloys in terms of consumer satisfaction, stating that while consumers admired the beautiful neutral color 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, & Gilmanⁱⁱⁱ of Stuller, Inc, one of the largest jewelry manufacturers in the United States, asserted the need for a new casting alloy. 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 historically used in platinum jewelry production prior to World War II. They were aware of the widespread use of 950 PtCo for jewelry 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 950 PtRu, 900 PtIr, and 950 PtCo.

This pursuit by Todd et al. to identify an alloy that performed better than PtRu and PtIr led to their conclusion that 950 PtCo was superior from raw casting through final polish, both in terms of polishing time and the presence of porosity. This research made 950 PtCo 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"^{iv} by Canadian metallurgist Greg Normandeau and co-author David Ueno. In this paper, Normandeau and Ueno argued the need for an alloy that would fulfill a long list of desirable attributes when investment casting. These included form filling, recycle ability, resistance to formation of oxides or brittle compounds, color, 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 chosen by a designer. Like Kretchmer, an analysis of alloy performance beginning with casting and carrying 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 summary, it is clear that none of these authors were very satisfied with the casting quality and wear resistance of the leading platinum jewelry alloys cast in North America during the nineties. Notably, these alloys remain the same today, with the exception that 950 PtCo has gained a significant, (although still minority) share of the market. Although there are certainly a greater number of alloys present on the market than in the mid-nineties, none have managed to solve all the problems that have historically challenged manufacturers and consumers. Even 950 PtCo, widely held to be the best casting alloy in terms of solidification characteristics, continues to receive low marks from bench jewelers and retailers due to its oxidation, magnetic properties, and minimal hardness when compared to most karat golds.

Room for Improvement

In 2007 TechForm Advanced Casting Technology conducted a survey of ten high-profile designers, custom jewelers^v, and retailers to determine what type of platinum casting defects were most frequently experienced. Respondents were chosen only if they had experience with a number of casters in recent years, in order that the best snapshot of prevailing industry-wide concerns was achieved. In addition, only respondents that had experience with a variety of platinum alloys were contacted to be sure that the representative cross-section was also widely dispersed in this regard.

The casting defect reported most frequently in the survey was sub-surface micro-porosity emerging late in the polish process. Unfortunately, this is the point at which manufacturers have invested the most time and money, and therefore experienced the greatest financial loss. Other reported defects included poor reproducibility of detail, cracking, large internal voids, and shrinkage porosity under sprues. While the survey's intent was to focus strictly on casting defects, a significant amount of anecdotal evidence emerged in these conversations with manufacturers and retailers reflecting general concerns about hardness and platinum's challenge to hold a high luster. Based upon past publications and current trade feedback, it is clear that opportunities exist for meaningful improvements both in terms of the cost and quality of platinum jewelry castings.

The Cost of Quality

Given that the market price of platinum has risen from approximately \$400 per ounce in the mid-nineties to over \$1,400 as of this writing, the manufacturer's cost impact of sub-standard casting quality has skyrocketed. What may have been a mere annoyance in 1995 has become a monumental expense on the profit and loss statements for many platinum manufacturers. If product must be recast, the inherent metal loss in the casting process will be doubled. When surface quality is characterized by metal to mold reaction and porosity is pervasive, substantially more platinum will be lost or transformed into refining dust than would be the case with a high quality casting. The extreme density of platinum means that even tiny amounts of the metal lost to inventory shrinkage in the manufacturing process have an enormously high cost.

In addition, competition from inexpensive foreign labor looms large over the comparatively high labor rates for bench jewelers in the western world. Losses in efficiency associated with poor casting quality take on new importance when companies try to compete with product coming from low wage countries in the developing world. Given that a poor quality platinum casting can add several labor hours to the manufacturing cycle for a single ring, these costs are substantial indeed for the developed countries, whether one is a high volume manufacturer or a small custom jeweler.

Taken as a whole, the combination of poor casting quality and high labor rates can drive manufacturers' margins down substantially. In addition, designs that have been welded, soldered and blended multiple times may suffer in terms of the quality of the finished piece. Given that platinum is generally purchased as a lifetime investment at a premium price, consumer expectations are naturally high when it comes to quality and longevity of wear without failures related to the metal.

Alloy Comparison Studies

In searching the literature for past studies we found a surprising lack of metallography or other hard evidence of alloy solidification behaviors accompanying them. The previously mentioned study by Todd et al., contained a small sampling of metallographic work on sprue sections for 950 PtCo, 950 PtRu, and 900 PtIr. More recently, Klotz and Drago published a larger number of metallographic cross sections for 950 PtCo and 950 PtRu in the 2010 Santa Fe Symposium proceedings^{vi}. Even with this more recent effort to generate hard data on solidification characteristics by alloy, much more is needed for a comprehensive understanding of different alloy chemistries in a variety of geometries. Jewelry designs are becoming increasingly complex with the wide use of CAD/CAM for model creation, and a deeper understanding of what this means for the internal metallurgical quality of platinum castings is necessary to assure a high quality product. Cross sections of casting trees or experimental geometries that do not reflect the realities of typical jewelry geometries, while interesting and informative, will necessarily be limited in the scope of their application.

The metallographic study that follows is a first step in a direction closer to actual jewelry geometries, while still maintaining the tight control factors necessary to learn critical information about alloy solidification behaviors specific to different chemistries.

Comparative Study of Alloy Solidification Behaviors

Several alloys were chosen for this study, based largely on the frequency of their use in North America. The table below lists some basic property data for these alloys.

Table 2 Common platinum alloys used in North America – basic property data

Alloy composition	Melting Range* °C	Hardness HV as-cast	Included in Studies Part I/II
950Pt 50 Co	1655-1680	135	I + II
950Pt 50 Ru	1780-1795	130	I + II
900Pt 100 Ir	1780-1790	110	II
950PtPd+	1620-1685	130 soft, 220 hard 150-200**	I
950PtRu+	1710-1750	180	I
950PtCo+	1640-1670	175	II

* Melting range is derived from both data found in the literature and alloy supplier information. These data originate from different methods of determination and therefore are not always consistent.

** This is an age-hardenable alloy. Therefore, hardness depends on cross sectional dimensions and casting process parameters. We observed large scatter in our trials (as shown in the indicated range) with an average value of ~ 170 HV.

The experimental study was divided into consecutive Parts I and II. The majority of the casting experiments were carried out at TechForm Advanced Casting Technology using Linn High-Therm centrifugal casting machines with induction heating. The machines are equipped with optical pyrometers for temperature control and have 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 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, depending upon the specific liquidus temperatures of the different alloys.

The casting trials for Part I were carried out with the aim of comparing the solidification behaviors between four 950 platinum alloys: 950 PtCo, 950PtRu, and two typical representatives of the hard platinum alloys available on the market designated 950PtRu+ and 950PtPd+. For alloys that are marketed under trade names that do not disclose all elements, we simply use the plus sign to indicate the presence of undisclosed elements.

The geometry chosen for Part I testing was a very uniform and flat test coupon. For high melting alloys this type of geometry is ideal for encouraging shrinkage porosity since solidification, even in a heavily sprued piece, will force the cooling casting to feed on itself when it cannot continue to solidify in a directional manner. Geometries that transition smoothly and gradually from thick to thin in one direction are optimum; those that are very uniform and heavy in mass are known to challenge solidification. The test coupon was sprued according to best practices for minimization of shrinkage porosity (thick, multiple sprues) and cast samples were submitted for metallographic analysis at the Legor R&D lab. The results are shown in detail in Figure 1.

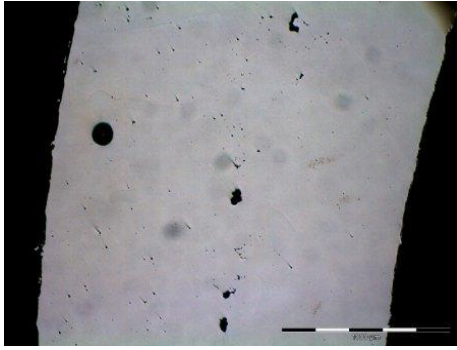


Fig 1a Pt950 Co

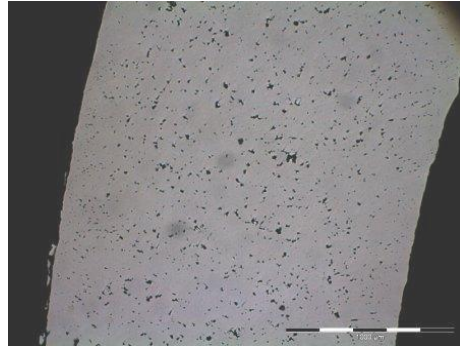


Fig 1b Pt950 Ru

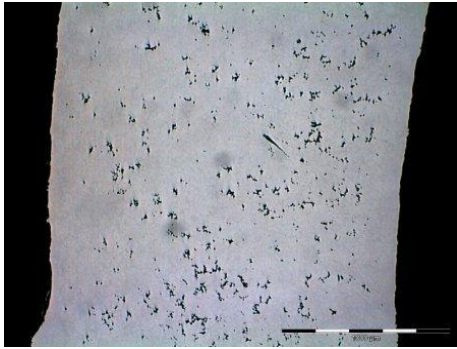


Fig 1c Pt950 Pd+

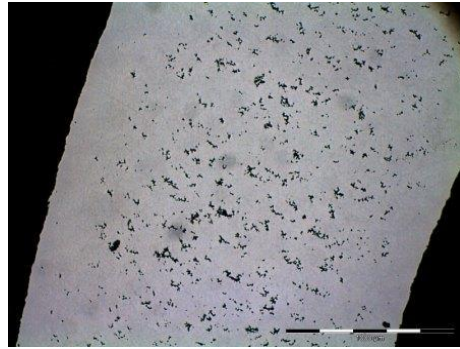


Fig 1d Pt950 Ru+

Results and Conclusions: Part I

950 PtCo had by far the lowest amount porosity observed, consisting of very small amounts of shrinkage porosity (irregularly shaped cavities) and some gas porosity (spherical cavities) (Figure 1a). Some of the pores were localized along the centerline of the ring shank. In contrast, 950 PtRu had a comparably large amount of shrinkage porosity that was fairly uniform in distribution throughout the piece (Figure 1b). Both of the hard 950 Pt alloys had a high level of shrinkage porosity comparable to what was observed in 950 PtRu (Figures 1c & d) with 950 PtRu+ performing somewhat worse than 950 PtRu for this particular pattern. Some overlap with gas porosity is also present for 950 PtRu, and is also present, but less obvious, for the two hard platinum alloys.

Most significant is the strikingly low level of shrinkage porosity for 950 PtCo in comparison to 950 PtRu and the two hard platinum alloys. This finding is consistent with some reports from the earlier literature cited above. Interestingly, the presence of large amounts of hardening elements or other non-precious base metals in the hard platinum alloys based on PtRu or PtPd does not seem to improve the solidification behavior and susceptibility to porosity.

As demonstrated by Klotz and Drago, the different thermal properties of investment materials can influence solidification behavior. Their results show that for a given alloy, pattern geometry and casting process the amount of shrinkage porosity will to some extent depend on the type of investment material. However, the review of previous literature as well as the results of the present study suggest that considerably more powerful in this regard are the specific alloy compositions that result in appreciably different physical properties and solidification characteristics. This in turn leads to a different susceptibility to porosity quite independent from the investment material. Based on computer simulation work done for gold and silver alloys, it was concluded that alloy properties like thermal conductivity and the so-called heat of solidification (heat that is released when the metal freezes) can significantly influence shrinkage porosity. High values for these parameters slow down the solidification process and allow for a more directional solidification, and therefore less shrinkage porosity. Unfortunately, corresponding material property determinations and simulation work are not yet available for platinum. Nevertheless, based upon our observations of solidification behaviors of platinum alloys together with the known thermophysical properties of platinum, one can at least theorize that lower values likely exist for these key parameters and that some significant differences are present for the different alloys.

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 commonly known excellent fluidity and form filling properties of 950 PtCo in comparison to 950 PtRu and other alloys would suggest better feeding properties during solidification. As seen in Figure 1, the results for 950 PtCo lend strong support to this claim.

Lastly, alloying additions of base metals used as hardening agents usually shift the melting range to lower temperatures and lead to a broader melting range. While the latter may be considered helpful to support directional solidification because it leads to an increase in solidification times, it has also been observed as detrimental; chaotic behavior occurs during solidification that complicates feeding, resulting in intersecting dendrites and more complex solidification microstructures.

In search of solutions to the high levels of shrinkage porosity seen in the hard platinum alloys, R&D work at the Legor lab confirmed that significant amounts (2-3 wt %) of Ga and/or other base metals are typically needed to raise the hardness of 950 platinum alloys into a desired range of > 160 HV, a number consistent with the alloy compositions and hardness values of presently known hard platinum alloys. It turned out, however, that comparably small additions (~ 1 wt %) to 950PtCo can already shift the hardness values above 170 HV. Consequently, an alloy with a corresponding 950 PtCo+ composition was included in Part II of this experimental study.

Results and Conclusions: Part II

Part II of the study focused on a comparison of the solidification characteristics of 950 PtCo, 950 PtRu, 900 PtIr, and a new chemistry for a hard 950 PtCo+ alloy. A new test geometry specifically designed to encourage directional solidification was used for this part of the study. The graduating thicknesses are shown in Figure 2a & b below, 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 jeweler's saw. It is worth noting that such a change in geometry can influence solidification.

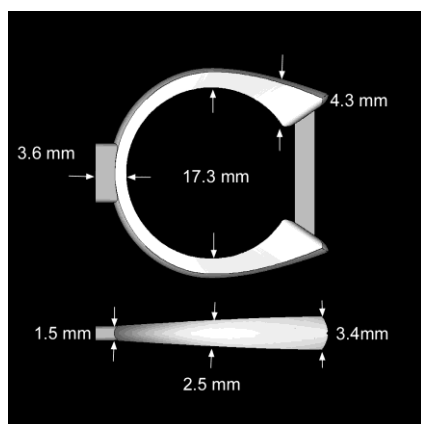


Fig 2a Single Bottom Sprue

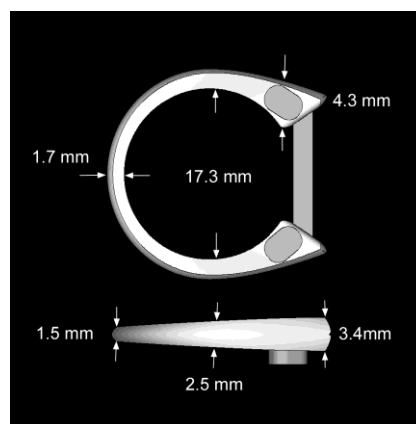


Fig 2b Double Top Sprue

The casting parameters for our trials are shown below. 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 optimum in a directionally solidified geometry, aims to depict a best-case scenario for solidification in each particular alloy.

Table 3 Casting parameters – Part II

CASTING PARAMETERS - PART II						
<u>Alloy</u>	<u>Sample Type</u>	<u>Sprue Type</u>	<u>Flask °C</u>	<u>Pour °C</u>	<u>Atmosphere</u>	<u>Investment</u>
Set A						
950PtCo	Shank	Single Bottom	850	1850	argon only	shell
950PtRu	Shank	Single Bottom	850	1900	argon only	shell
900PtIr	Shank	Single Bottom	850	1900	argon only	shell
950PtCo+	Shank	Single Bottom	850	1830	argon only	shell
Set B						
950PtCo	Shank	Double Top	850	1850	argon only	shell
950PtRu	Shank	Double Top	850	1900	argon only	shell
900PtIr	Shank	Double Top	850	1900	argon only	shell
950PtCo+	Shank	Double Top	850	1830	argon only	shell
Set C						
950PtCo	Shank	Double Top	850	1740	vac / argon	shell
950PtRu	Shank	Double Top	850	1800	vac / argon	shell
900PtIr	Shank	Double Top	850	1800	vac / argon	shell
950PtCo+	Shank	Double Top	850	1700	vac / argon	shell
Set D						
950PtCo	Shank	Double Top	850	1850	argon only	high speed dental
950PtRu	Shank	Double Top	850	1900	argon only	high speed dental
900PtIr	Shank	Double Top	850	1900	argon only	high speed dental
950PtCo+	Shank	Double Top	850	1830	argon only	high speed dental

* The vac/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.

A first overview of the results (shown in detail in Figures 3-6) suggests that independent from specific casting parameters, 950 PtCo performs the best from a shrinkage porosity standpoint and 950 PtRu performs the worst. The 900 PtIr is very close to 950 PtCo, and the hard 950 PtCo+ alloy is slightly inferior to 950 PtCo with small but consistently higher levels of micro-porosity.

The comparison of results from set A, Single Bottom sprue system, and set B, Double Top sprue system, simply demonstrate that comparably thick and multiple sprues attached to heavy sections of the pattern are mandatory for obtaining acceptably low levels of porosity in 900 and 950 platinum castings. With the Single Bottom sprue system, all alloys apart from 950 PtCo 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). Consistent with the results from Part I, 950 PtRu still 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 of porosity is observed for 950 PtRu (Figure 5b), the corresponding improvement for 950 PtCo+ is low (Figure 5d) and the opposite is observed for 900 PtIr (Figure 5c). For 950 PtCo the porosity is lowered in most areas, but two huge gas pores pop up on the ring shank (Figure 5a).

It should be acknowledged that the potentially lower and less reliable reading on the pouring temperatures for the samples of set C (see above) may have contributed to the apparent inconsistency in results. However, it may be cautiously concluded that a combination of poor melting atmosphere and excessive time at a molten state in the crucible can contribute to the larger porosity level that is usually observed for 950 PtRu.

In contrast to this, the fact that gas porosity still occurs in significant amounts for 950 PtCo and 900 PtIr, 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 (be it air or argon) through the mold material play an important role (Figures 6a-d). Overall a lower amount of gas porosity is observed for all alloys, especially for 950 PtCo and 900 PtIr in the samples for set D. It is assumed that the dental investment has higher gas permeability than a dense shell mold 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 same for either a shell mold system or the high speed dental investment.

It must also be noted that castings from the high speed dental investment exhibit a much rougher surface finish due to the lower thermal stability of this investment in comparison with the shell system. This condition, combined with the fact that high-speed dental investments are typically only good for very low pour weights, present significant trade-offs to be considered when using these materials in a production environment.

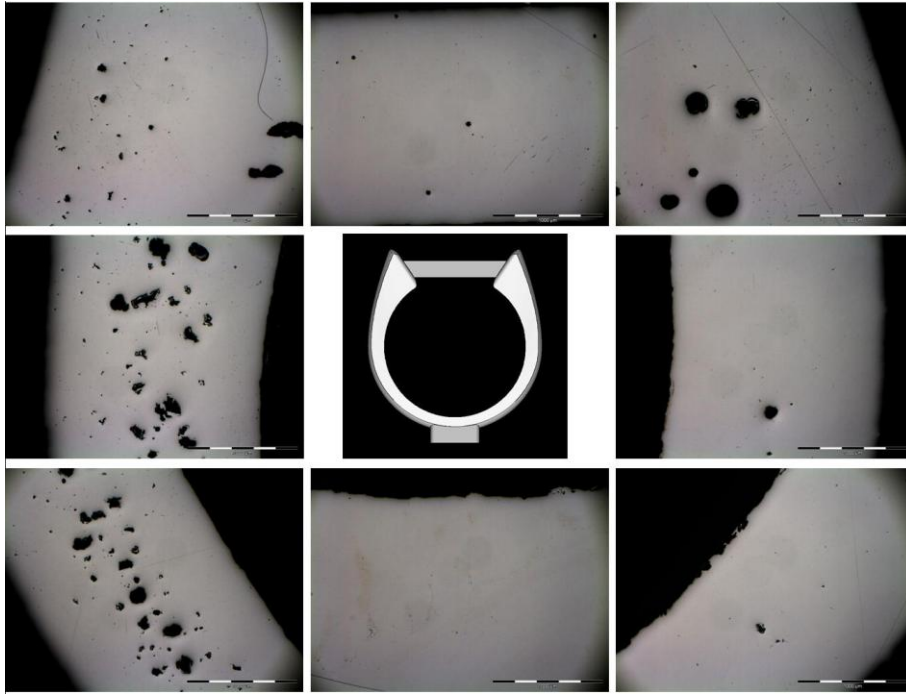


Figure 3a Pt950Co, Set A , single bottom sprue

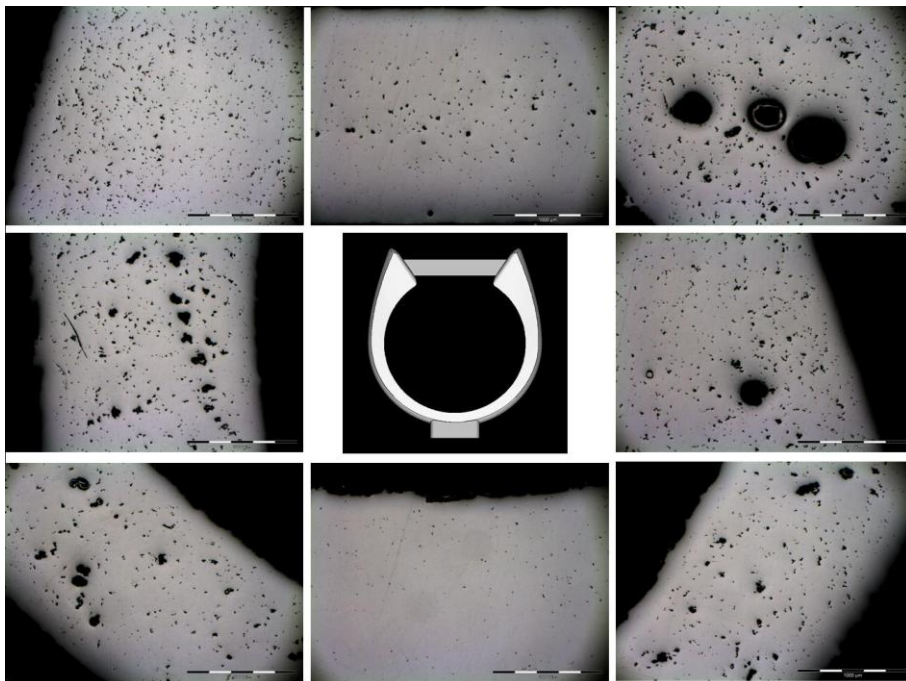


Figure 3b Pt950 Ru, Set A single bottom sprue



Figure 3c Pt900Ir, Set A, single bottom sprue

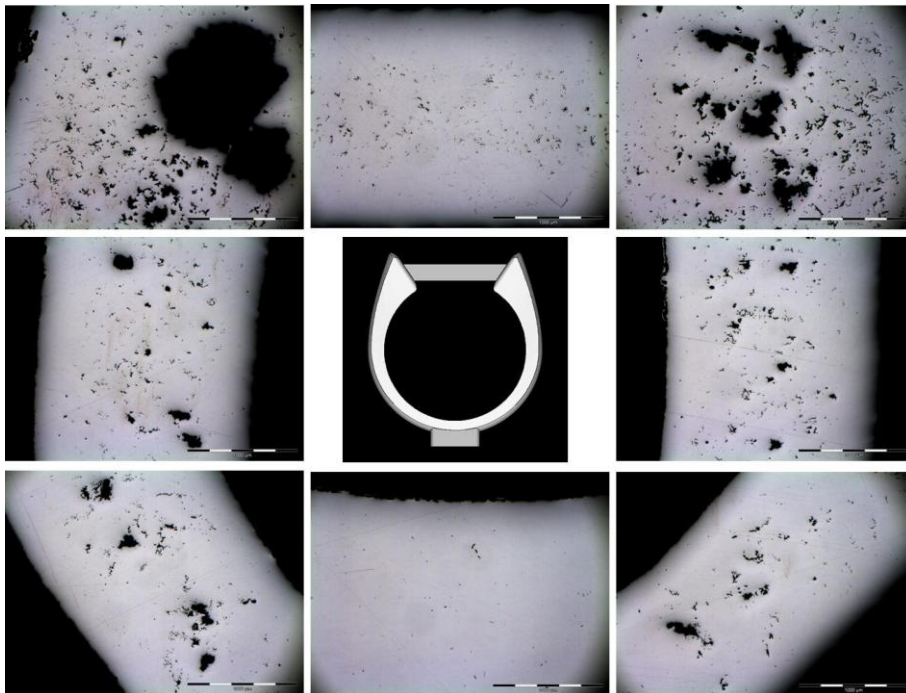


Figure 3d Pt950Co+, Set A, single bottom sprue

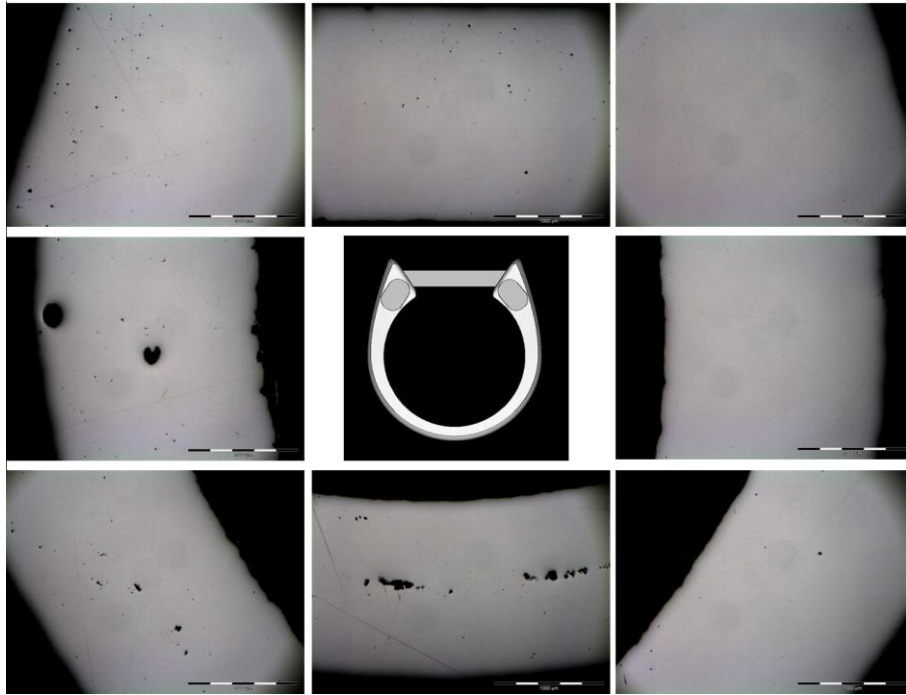


Figure 4a Pt950Co, Set B, Double Top sprue

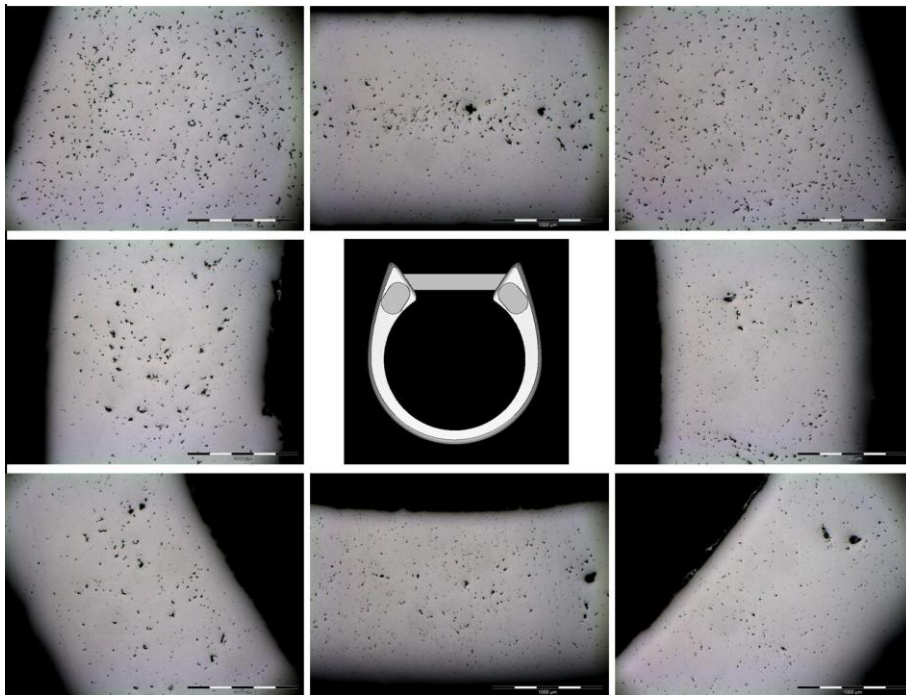


Figure 4b Pt950 Ru, Set B, Double Top sprue

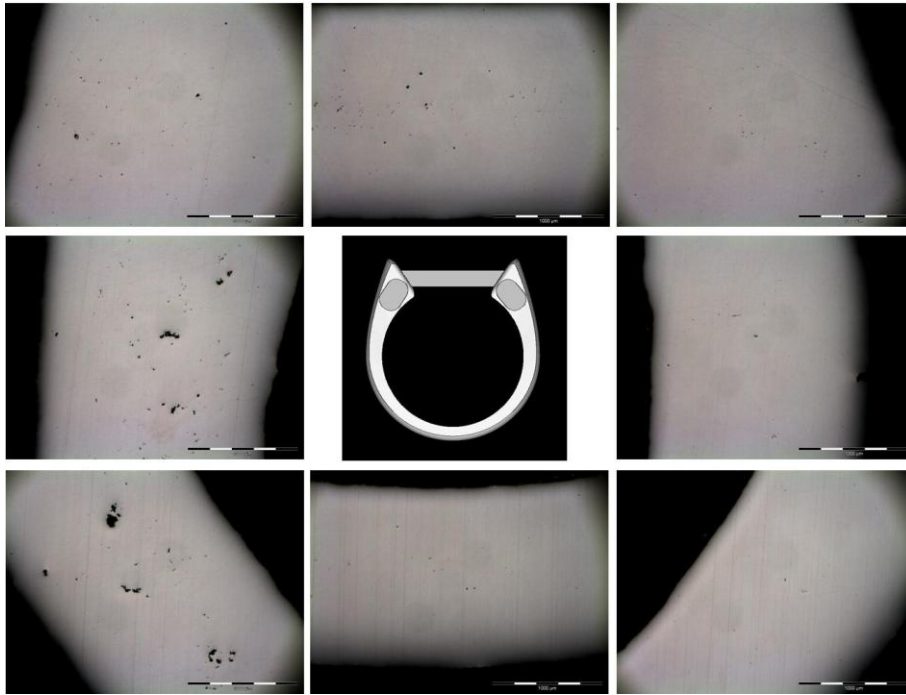


Figure 4c Pt900Ir, Set B, Double Top sprue

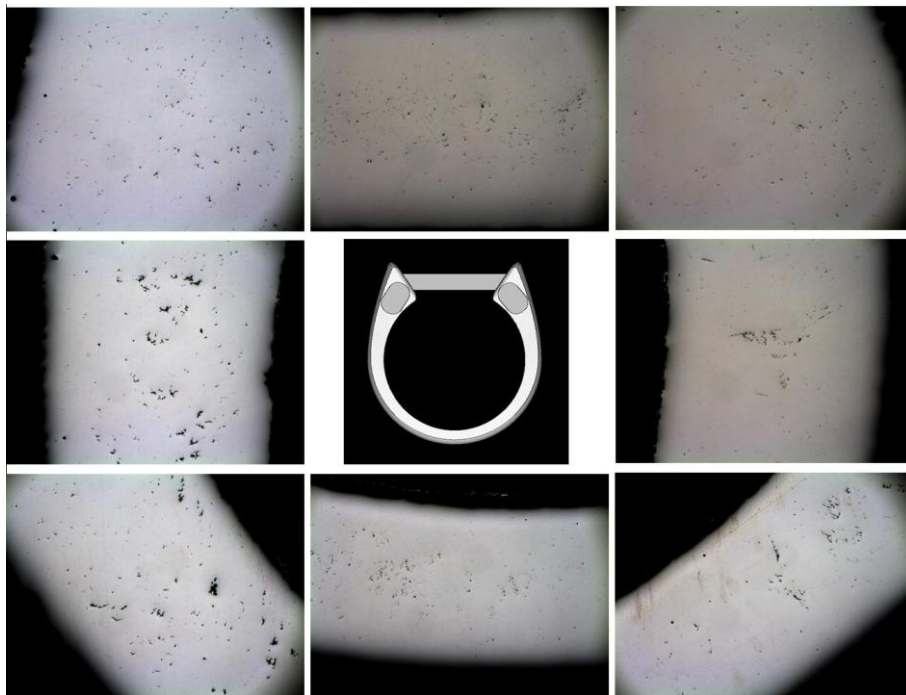


Figure 4d Pt950Co+, Set B, Double Top sprue

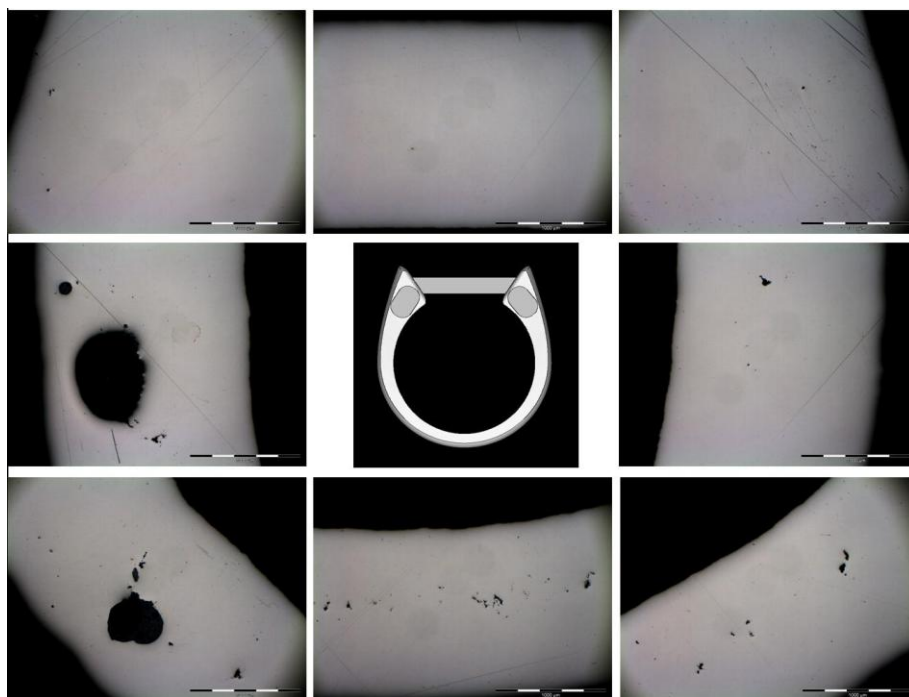


Figure5a Pt950Co, Set C , Vacuum/Argon

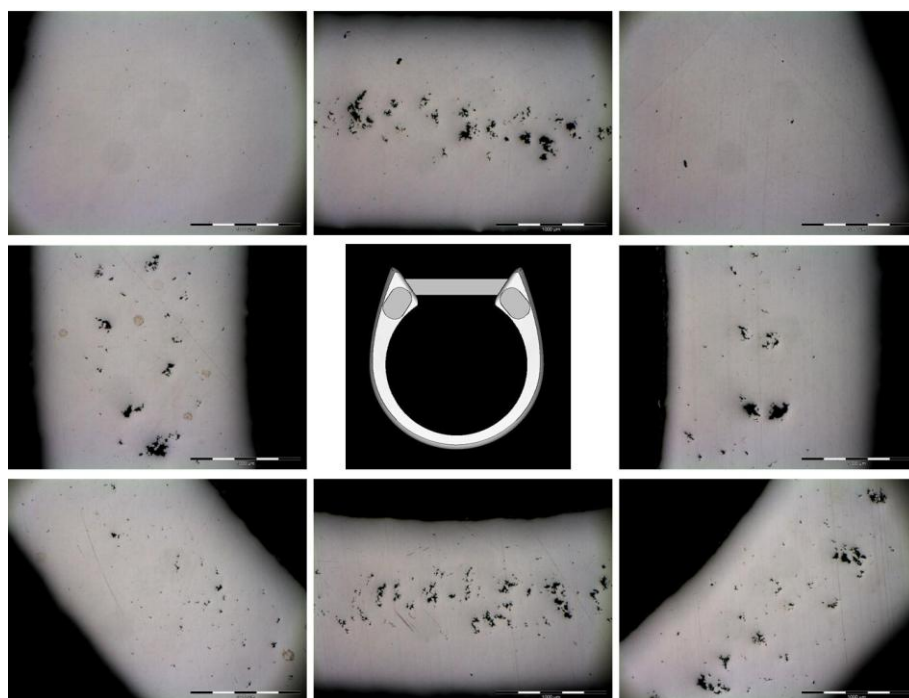


Figure5b Pt950Ru, Set C , Vacuum/Argon

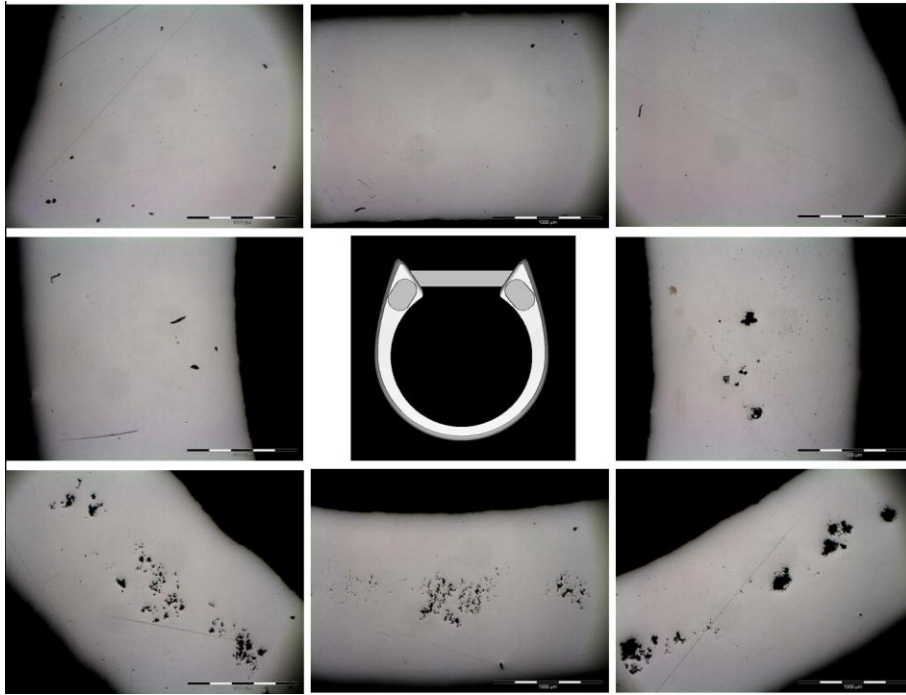


Figure 5c Pt900Ir, Set C , Vacuum/Argon

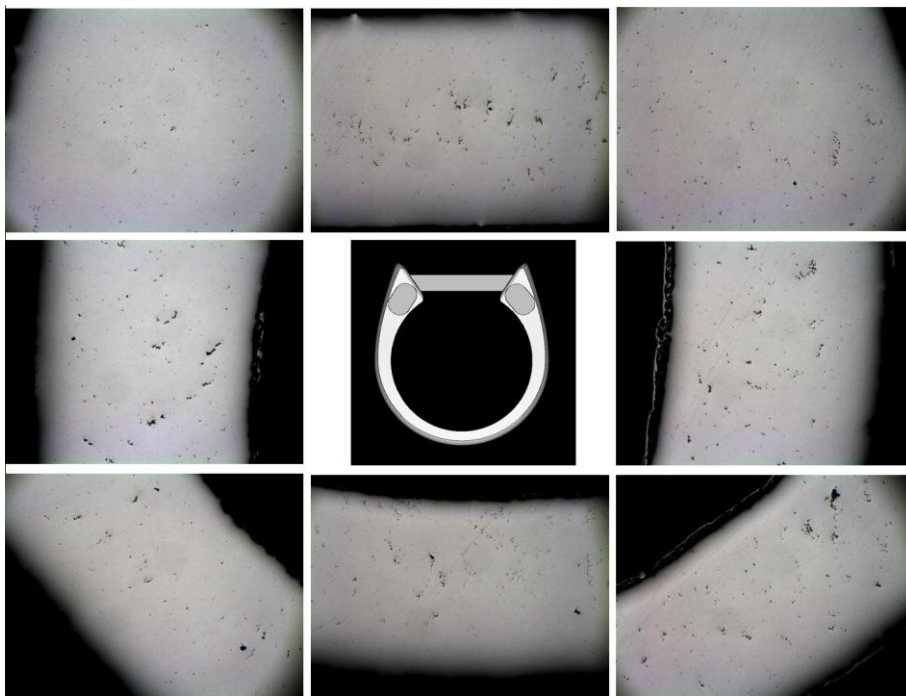


Figure 5d Pt950Co+, Set C , Vacuum/Argon

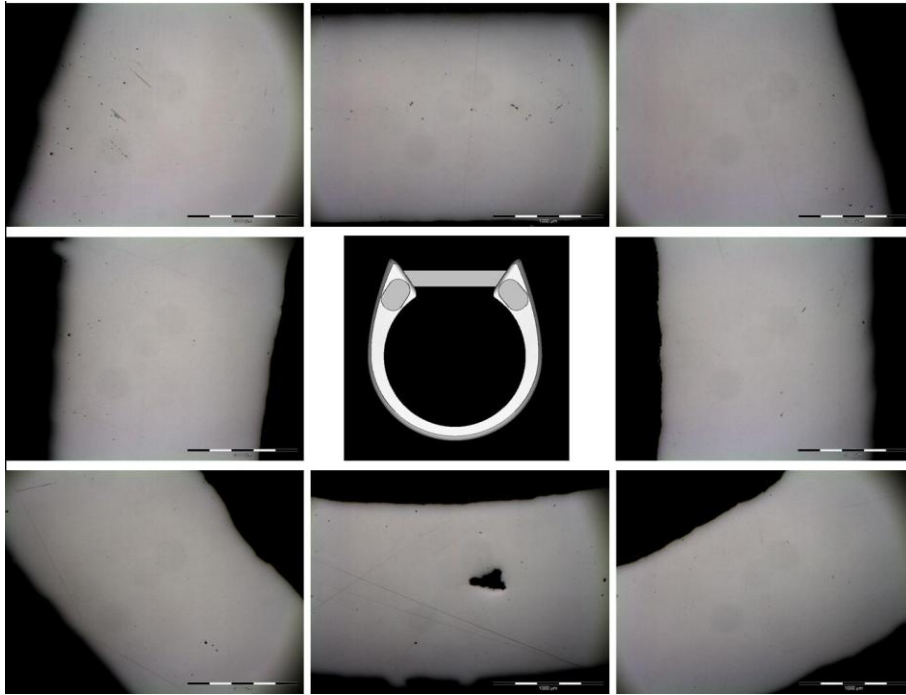


Figure 6a Pt950Co, Set D , high-speed dental investment

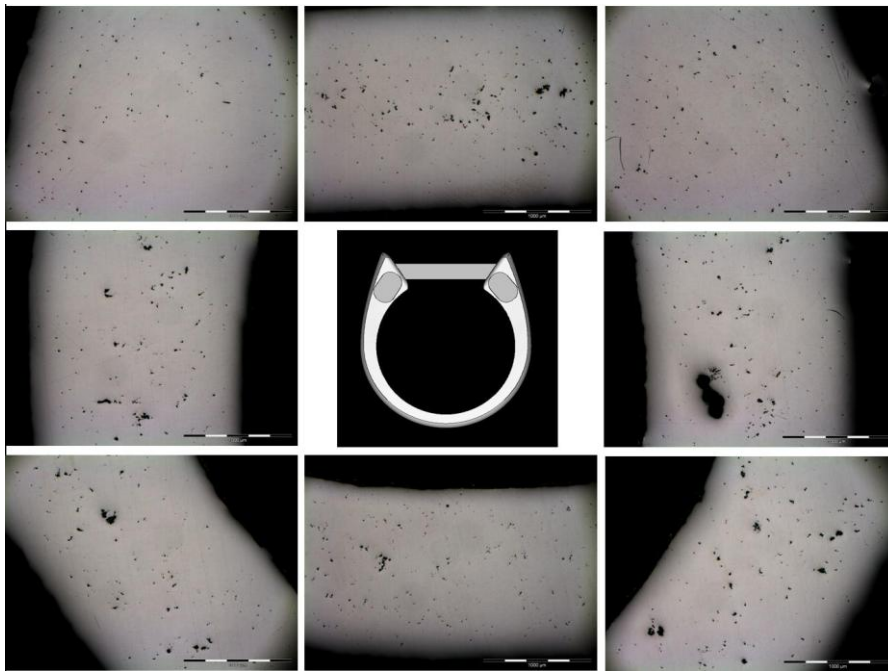


Figure 6b Pt950Ru, Set D , high-speed dental investment

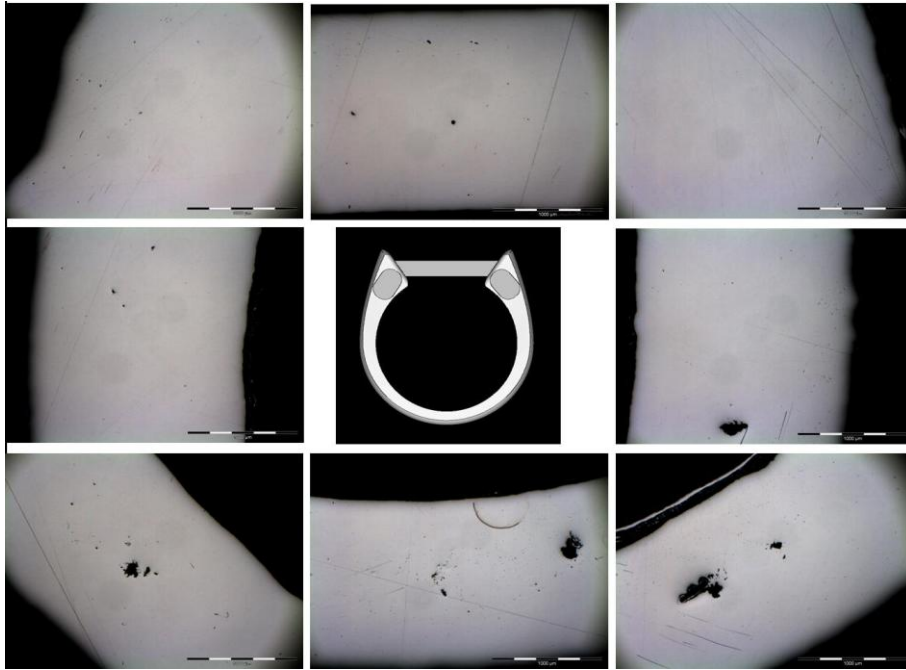


Figure 6c Pt900Ir, Set D, high-speed dental investment

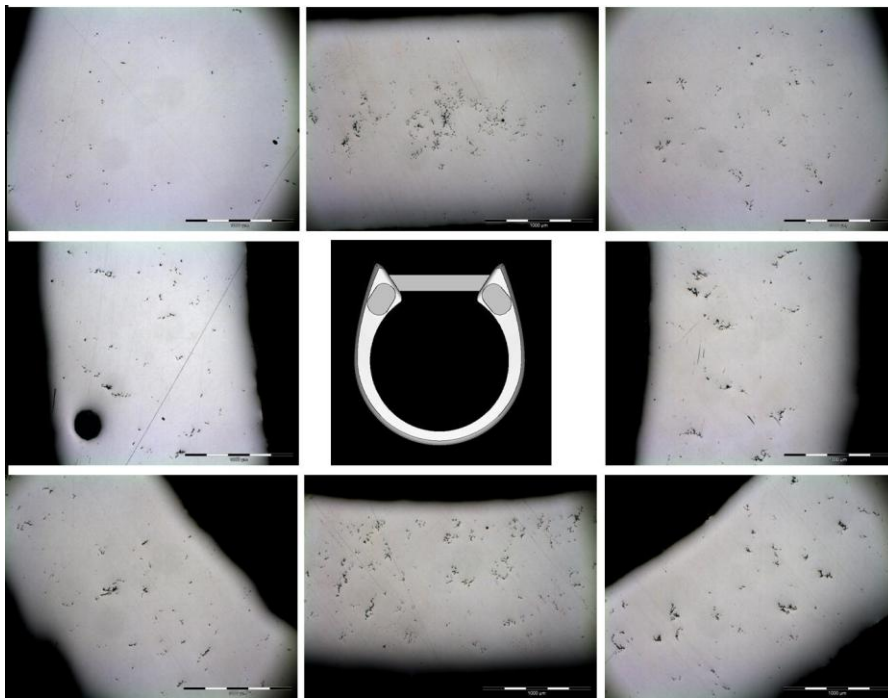


Figure 6d Pt950Co+, Set D, high-speed dental investment

Further properties of the hard 950 PtCo+ alloy

The detailed metallographic analysis raises some hope that porosity levels nearly as low as those for 950 PtCo can be consistently obtained in a significantly harder alloy based on 950 PtCo+. The other hard platinum alloys show a greater tendency towards uniform and scattered shrinkage porosity close to the polishing surface, while the 950PtCo+ exhibits a smaller amount that also moves toward the centerline and remains further away from the polishing surface. As discussed earlier, it is assumed that the comparably low level (~ 1 wt %) of alloying additions that is required to increase the hardness of 950 PtCo is essential.

Another very interesting and highly beneficial aspect of this alloy is that with ~1% alloying addition the 950PtCo+ loses its ferromagnetic properties. In the past, magnetism has contributed significantly to the low acceptance of 950 PtCo 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 jewelry 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 950 PtCo so that moderately higher (+20-30°C) pouring temperatures are required for the hard 950 PtCo+ to obtain similarly good form filling results as for the standard 950 PtCo alloy. Both Co containing alloys easily fill a test grid pattern at the standard pouring conditions used in this study, while 950 PtRu and 900 PtIr fail to achieve complete fill (Figure 7).



Fig7 Grid fill tests

Another important aspect for any platinum alloy is its recycle ability. We tested the 950PtCo+ alloy by performing a recasting “stress” test consisting of five recasting cycles of 100% scrap material. The resulting metal was completely ductile and experienced no change in hardness or increase in porosity. Furthermore, the alloy was tested to see how it would perform with a standard phosphate bonded investment in addition to the shell system and high speed dental investment. Similarly low levels of porosity were obtained for castings of the test geometry at the Legor R&D lab using a conventional 1-part platinum investment as shown in Figure 8 below. This section is an example from the first recasting cycle with 100% revert material.

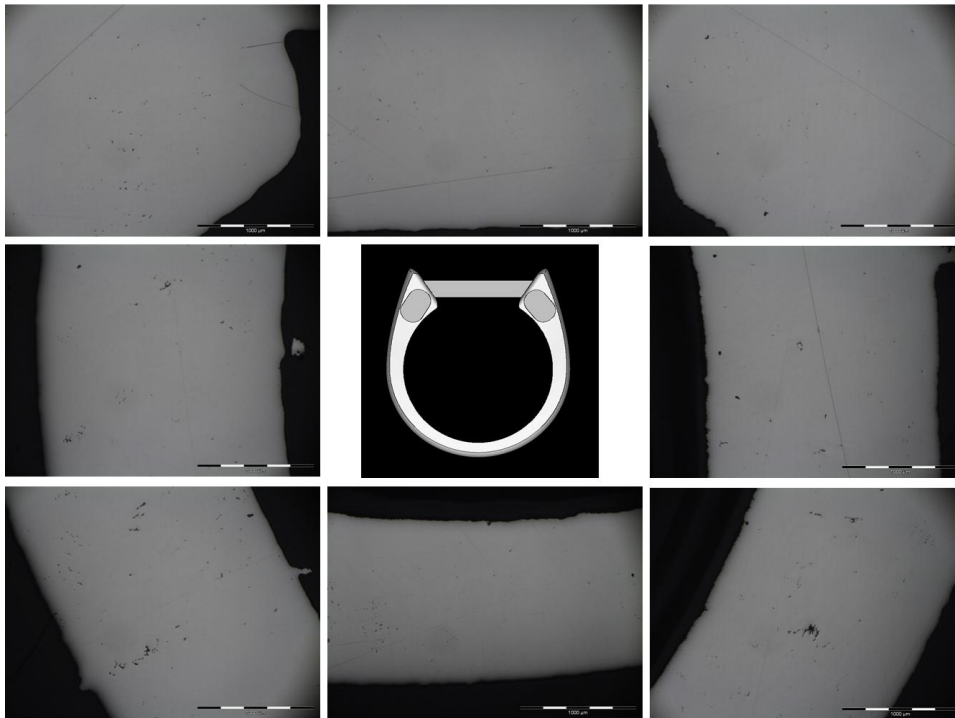


Figure 8 *Pt950 Co+; 1x recasting of 100% scrap material; 1-part platinum investment*

Finally, the etched microstructures shown in FIGURES 9a & 9b document that a smaller as-cast grain size is obtained for 950 PtCo+ when compared to 950 PtCo. The solidification microstructure changes from comparably large and columnar grains in 950 PtCo, to predominantly equiaxed, finer grains in PtCo+. The etched microstructures illustrate that the growth of columnar grains yields to the typical accumulation of center-line porosity in the case of 950 PtCo, while a more scattered distribution of microporosity is associated with the equiaxed solidification microstructure of 950 PtCo+.



Fig9a *grain structure Pt950 Co*

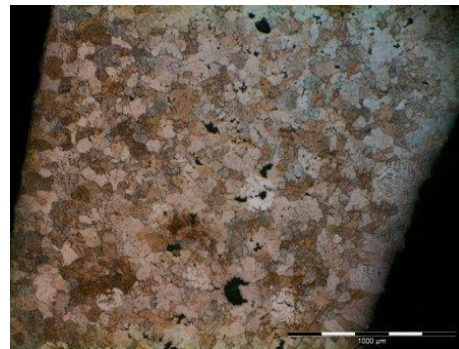


Fig9b *grain structure Pt950 Co+*

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, 950 PtRu, 950 PtCo, and 950PtRu+, 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 below (Figures 10a-c)

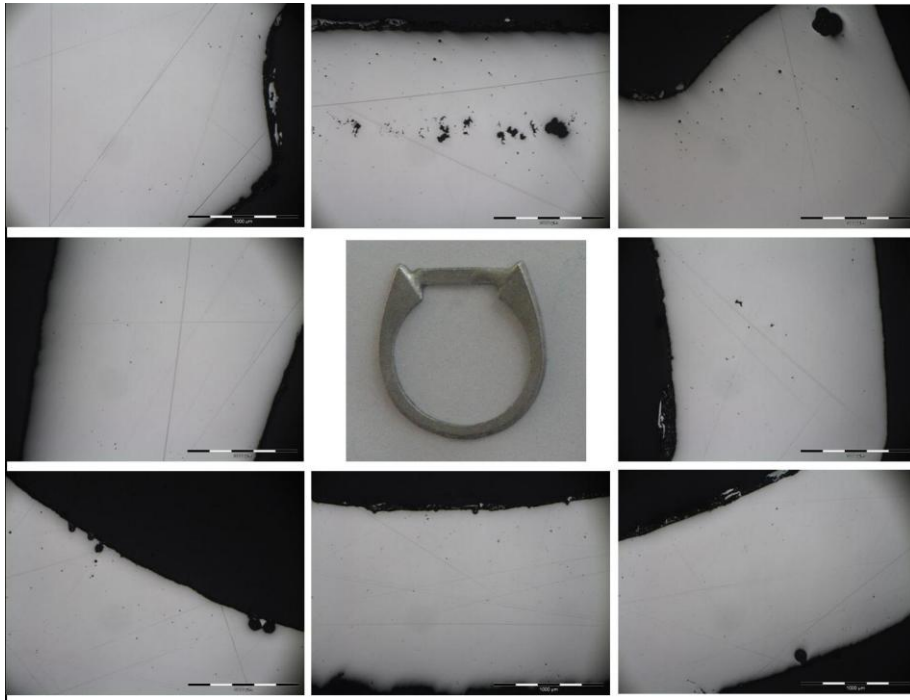


Figure 10a Trade casting Pt95Co

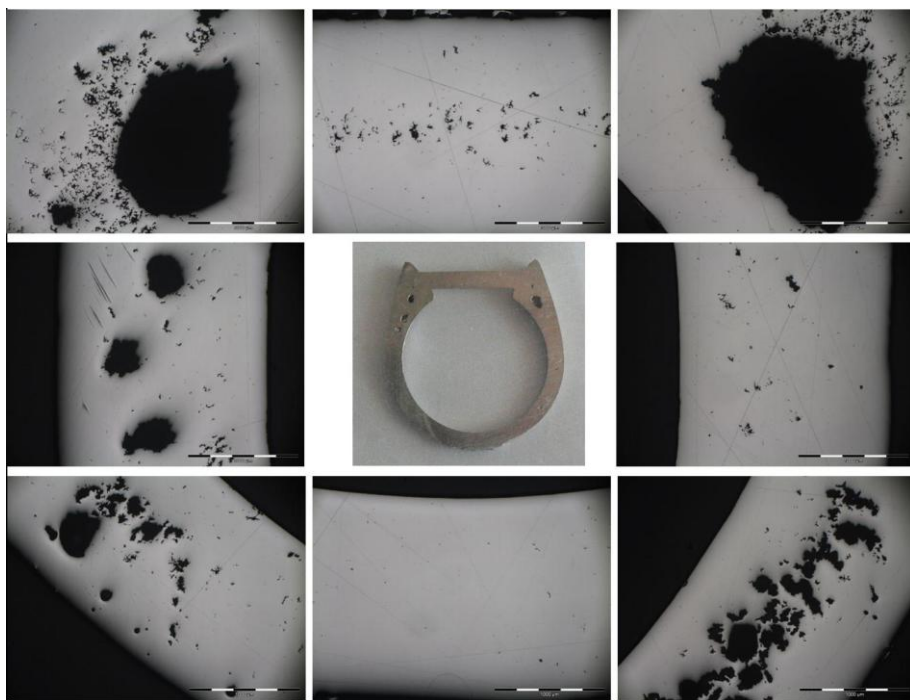


Figure 10b Trade casting Pt950Ru

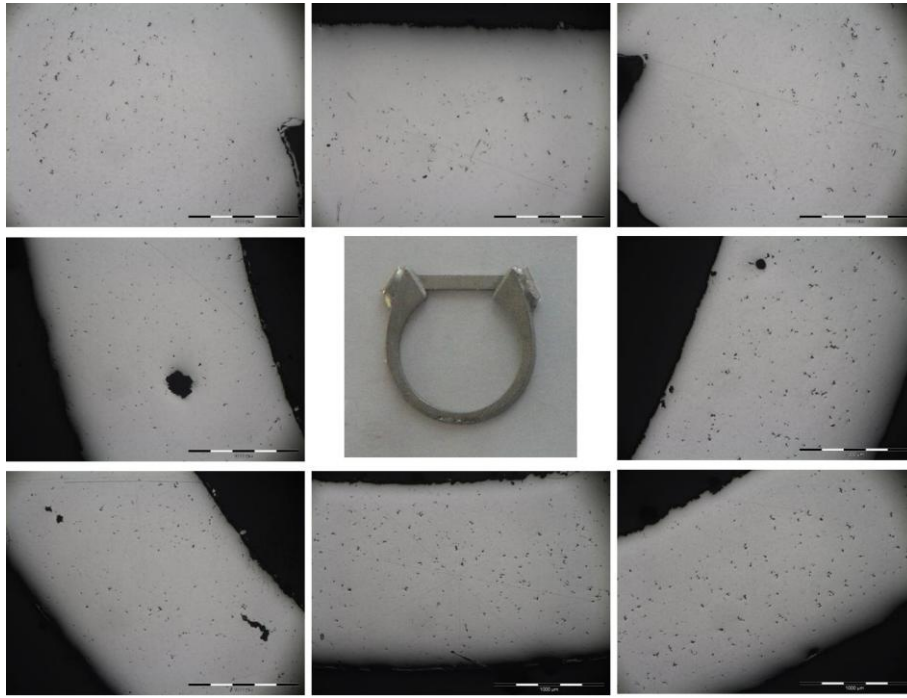


Figure 10c Trade casting Pt950Ru+

As we can see, the results for the 950 PtRu 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 950 PtCo and 950 PtRu+ alloys. For 950 PtCo no shrinkage porosity but some spherical gas pores are observed that accumulate in the centerline region as well as areas near the surface (Figure 10a). In the 950 PtRu+ 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 mold 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 confirmation that independent of the sprue system and the investment, the alloy's chemistry 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 that involved sending test samples of our Part II alloys to Bodycote^{vi}, a thermal processing company, for hot isostatic pressing. This high pressure thermal treatment, commonly referred to by its acronym "HIP" is a regularly used process on investment castings in quality-critical industries such as medical and aerospace. The HIP process involves placing the castings into a high pressure vessel for a specified period of time with inert gas at elevated temperatures. The result is densification, which results from a compressing of the metal in an environment and at a temperature that allows for the bonding of interior shrinkage cavities.

For this experiment we used the same test geometry and alloys as in Part II. 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 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).

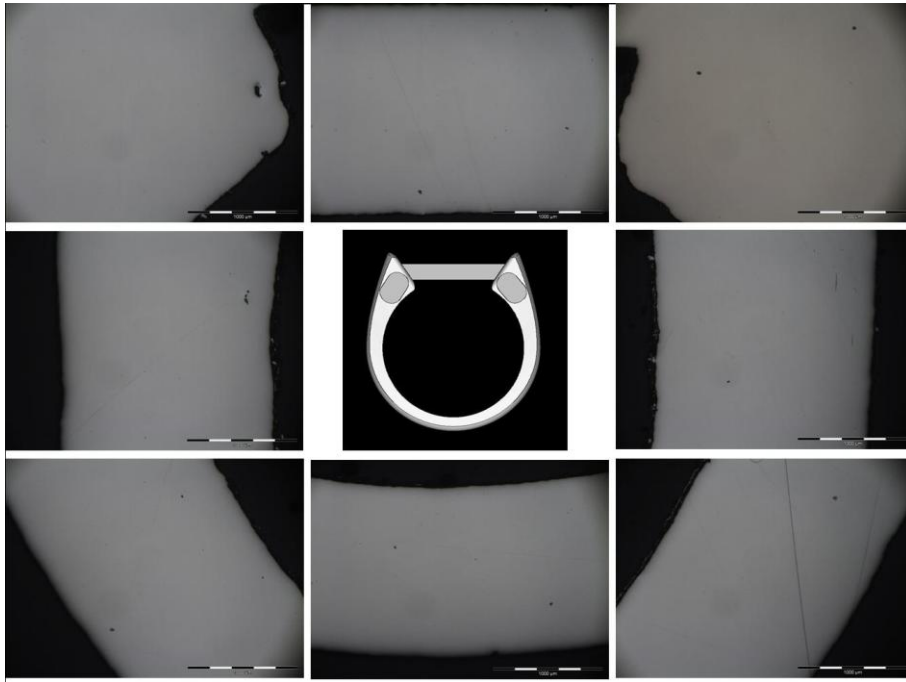


Figure 10a *HIP treated Pt950 Co*

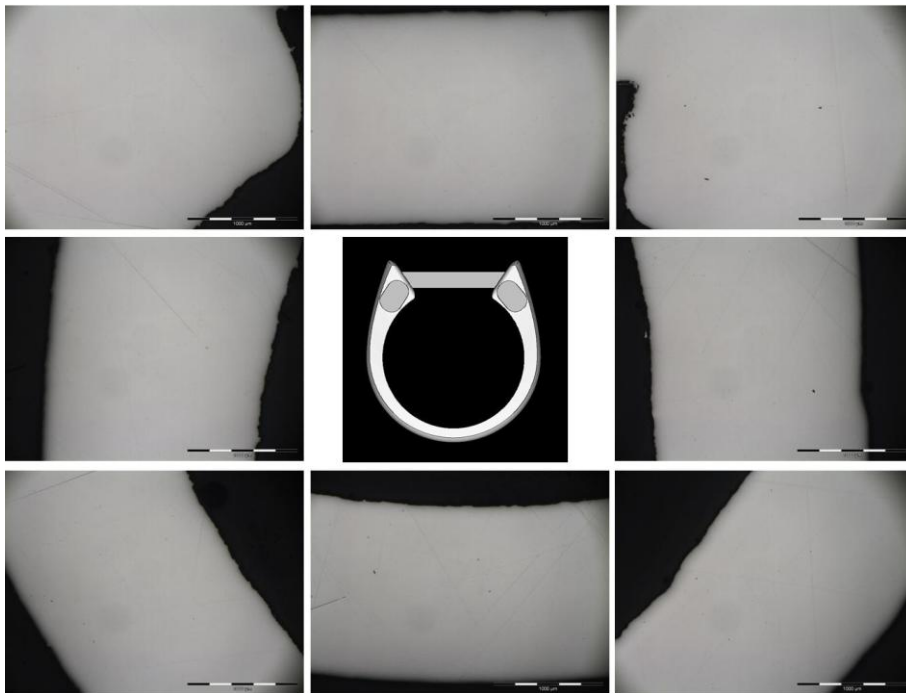


Figure 10b *HIP treated Pt950Ru*

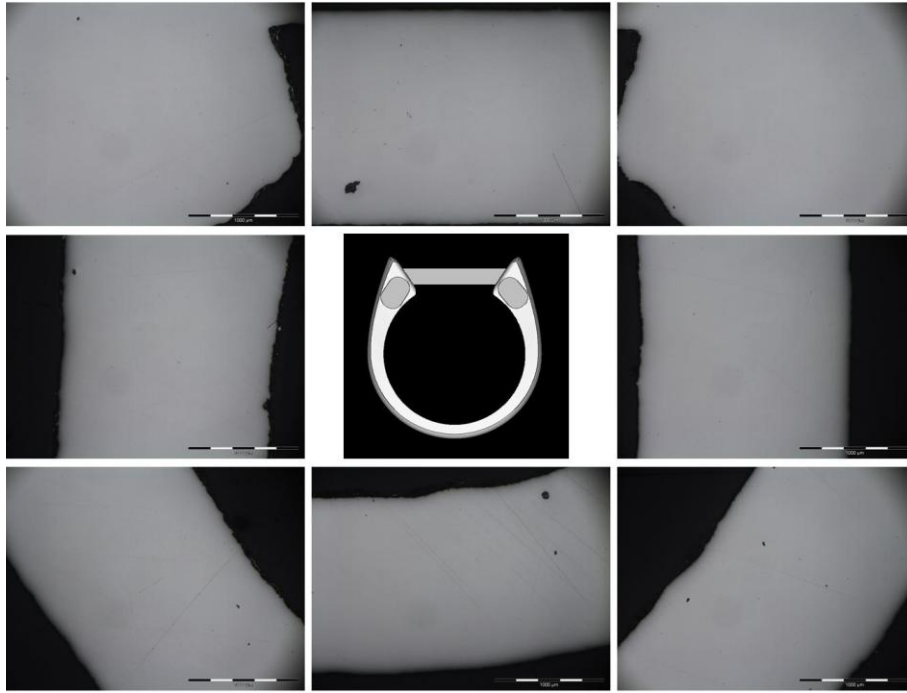


Figure 10c *HIP treated Pt900Ir*

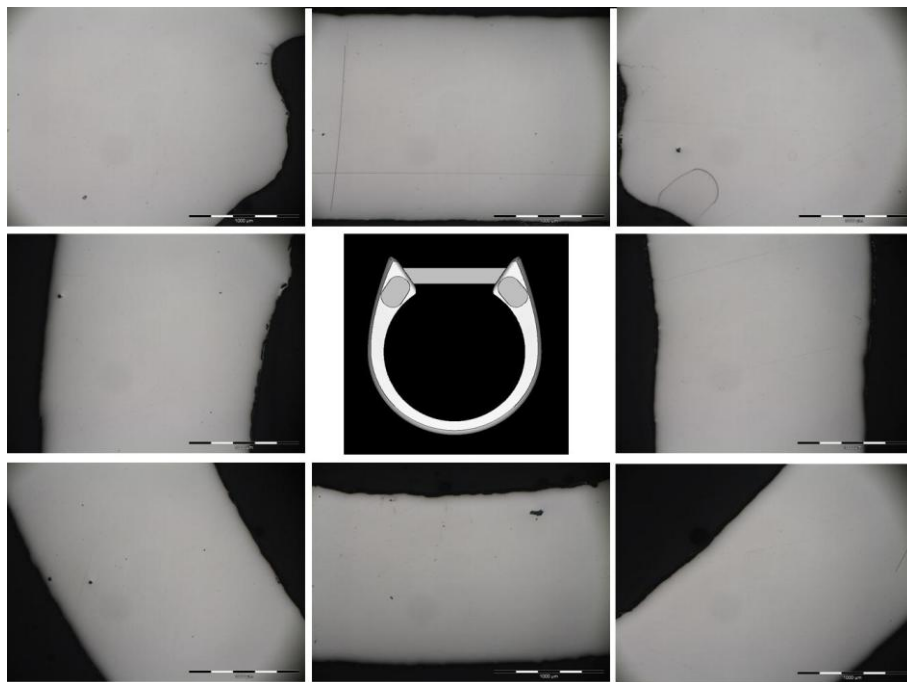


Figure 10d *HIP treated Pt950Co+*

Impressively, almost no porosity is left after the HIP treatment for all castings. Any micro-porosity was completely closed, while a few smaller cavities that are still present are probably the remainders of some larger gas pores which did not completely close during the HIP treatment.

Conclusion

Platinum jewelry 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 behaviors directly impact the polishing labor required to finish a jewelry article, and other characteristics such as ability to fill fine sections and hardness also affect the cost of bringing a quality product to market.

In looking back on the work from authors in the mid-nineties, it has become clear through our research that they were indeed true pioneers in the understanding of cast platinum alloys. They championed harder alloys to speed up polishing and improve the consumer's experience, while also distinguishing which alloys had inherent tendencies toward shrinkage porosity. The detailed metallographic work that has been done in this research confirms many of the assertions they made, with additional hard data demonstrating that 95Pt5Co exhibits not only superior form filling but also much lower shrinkage porosity in comparison with 95Pt5Ru. In addition, a greater understanding of the higher levels of shrinkage porosity that exist in the hard platinum alloys on the market also helps us to understand at least one of the reasons why these alloys have not as of yet been embraced by manufacturers.

It is our hope that through this research we have demonstrated that technical solutions exist towards improving the quality of platinum jewelry castings. Whether one finds a solution through the improved solidification of the PtCo based alloys or the use of hot isostatic pressing to densify and further harden shrinkage-prone alloys, opportunities for real and positive change exist.

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