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The Effects of Hot Isostatic Pressing of Platinum Alloy Castings on Mechanical Properties and Microstructures

Post processing of parts for jewellery and other applications

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The effects of hot isostatic pressing (HIP) on castings produced in a variety of platinum alloys was investigated. A number of benefits were observed, including a reduction in porosity and improvements to the microstructure and mechanical properties. Differences in the response to HIP of individual alloys is evaluated as well as some inherent limitations of the HIP process.

Introduction

In earlier research a better understanding of the solidification characteristics for a number of platinum-based alloys was established (1). The findings demonstrated a strong tendency toward the formation of shrinkage and gas porosity upon solidification, and HIP, a high-pressure thermal treatment developed as a densification process, was proven to be an effective method to minimise or eliminate this porosity.

While the previous results made it clear that porosity had been significantly reduced following the HIP process, the authors had not yet explored the full range of HIP's effects in terms of post-processed microstructure and mechanical properties. The goal of this new phase of research is to further our understanding by characterising the post-HIP effects on platinum based castings with respect to grain size and shape, chemical distribution and mechanical strength.

Overview of Hot Isostatic Pressing

Companies that build HIP equipment or perform the HIP process describe an isostatic press as something that forms and densifies powdered and cast materials using liquid or gas under extremely high pressure. Unlike mechanical force which compresses a workpiece from one or two sides, the isostatic pressure is applied

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uniformly on all sides of an object, eliminating internal porosity without changing net shape. Typical product improvements cited by the HIP industry are the elimination of internal voids, improvements in product consistency, and improvements in the soundness and mechanical properties of materials. The fundamental material change underlying these improvements is the attainment of a higher density material in comparison with its pre-HIP condition.

The isostatic nature of pressure in the HIP process as described above is key to maintaining the dimensional integrity of a casting during HIP; the pressure being equal on all sides lends to a uniform compression of the material with product dimensions typically remaining intact. Although, as seen in **Figure 1**, local deformations in the form of 'dimpling' can occur when the sizes of internal pores are extremely large and diffusion bonding collapses exterior surfaces inward. This difficult to feed thick-to-thin geometry for the channel band represents an extreme example of subsurface shrinkage porosity and is a powerful representation of the pore collapsing that can occur with HIP.

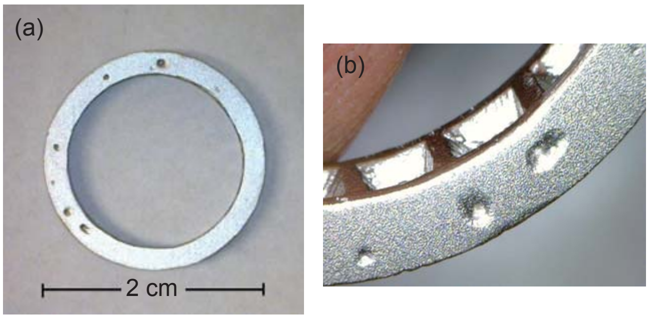

Fig. 1. HIP dimples in a 95Pt5Ru channel band

To better demonstrate how the HIP process works, **Figure 2** shows the schematic for a typical HIP unit. The unit contains a high temperature furnace enclosed in a pressure vessel. Parts are typically placed within the chamber in vertical layers with the use of graphite, steel or ceramic shelving to maximise load capacity. During operation the HIP chamber is first placed under vacuum, followed by flooding with an inert gas, usually argon, which is used to apply the isostatic pressure. The temperature and pressure is then ramped up and left to dwell for a specified period of time depending upon the material's properties. Parts become densified when the material's yield strength is surpassed, creating a plastic flow that forces internal voids to collapse under differential pressure. The internal surfaces of the voids diffusion bond together, increasing density and thereby improving the material properties. HIP unit sizes span from small laboratory size up to large-scale industrial. The unit shown in **Figure 3** is an example of a medium scale unit.

Not all metals will HIP effectively and the extent to which an alloy will respond to HIP is a function of its creep resistance. Creep is a solid material's tendency to move slowly and deform permanently under stress. In metals, creep increases with temperature and starts at approximately 30% to 50% of an alloy's melt temperature (2).The rate of creep is a function of temperature, the material's properties, and the amount of pressure that is applied. In order to achieve optimum material properties, the parameters used in a HIP cycle

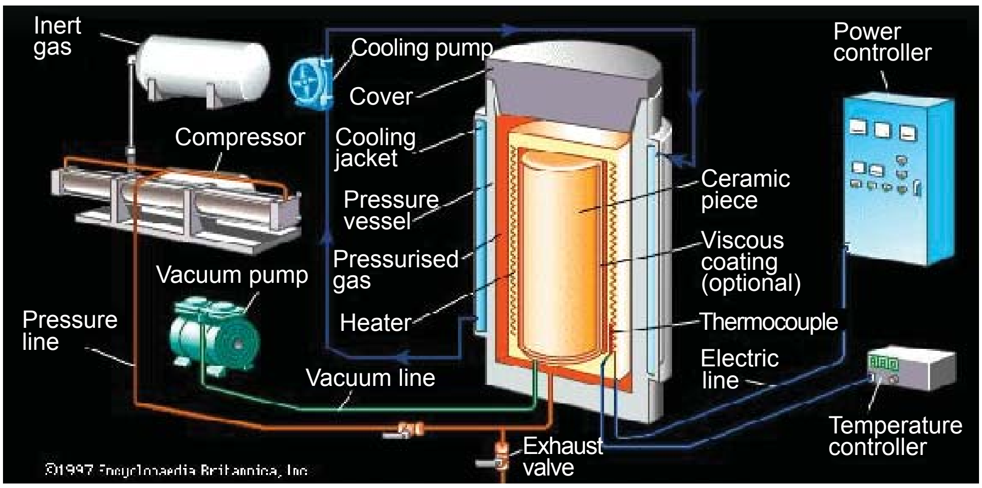

Fig. 2. Schematic of a typical HIP unit

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Fig. 3. HIP unit, courtesy Avure Technologies, USA

must be precisely dialled in according to the needs of the alloy. Typical parameters including both metals and ceramics will generally fall into the ranges shown in **Table I**.

Table I HIP Parameter Ranges[a]

Parameter	Typical lower limit	Typical upper limit
Temperature	500ºC	1400ºC
Pressure	7000 PSI	45,000 PSI
Dwell Time	2 hours	4 hours
Cooling Rate	1ºC per minute	100ºC per minute

[a]Courtesy Avure Technologies

Comparative Study of the Effects of HIP on Platinum Alloy Microstructure and Mechanical Properties

The goal of this research was to characterise post-HIP effects on castings with respect to grain size and shape, chemical distribution, and mechanical strength. The following sections report the methods used, results and conclusions.

Test Geometry

A tapered test specimen was chosen to assess microscopic porosity levels, density and hardness before and after HIP. As shown in **Figure 4**, the test specimen was designed to promote directional solidification with a single heavy sprue attached to the thickest end.

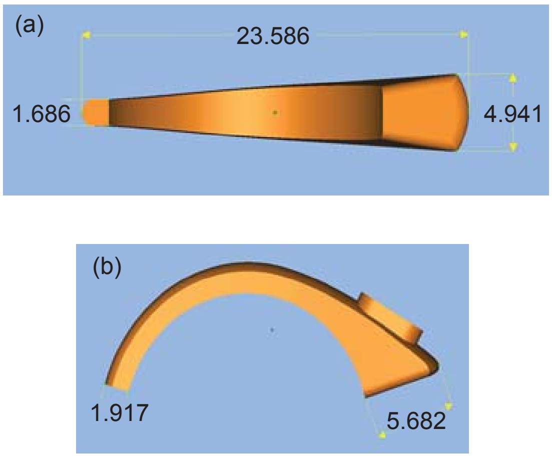

Fig. 4. Tapered test specimen (units in mm)

Casting Parameters

The casting parameters and conditions for these trials are shown in **Table II**. Standard pour temperatures, flask temperatures and firing curves were used. The flasks were cast using a centrifugal casting machine with induction heating and each tree contained two test geometries for each alloy. One casting was retained for as-cast sampling and the second casting was HIPed.

Table II Casting Parameters

Alloy	Pour temp., ºC	Flask temp., ºC	Casting condition
95Pt5Ru	1870	850	1 As-cast; 1 HIPed
90Pt10Ir	1870	850	1 As-cast; 1 HIPed
90Pt10Rh	1960	850	1 As-cast; 1 HIPed
95Pt5Co	1850	850	1 As-cast; 1 HIPed

Notes to Table II

(a) All patterns 3D printed for dimensional precision

(b) All trees were identically assembled with two samples per tree

(c) All flasks air cooled identically

(d) All alloys were HIPed in the same load

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Effects of HIP on Microstructure

Given the high levels of porosity seen in 95Pt5Ru and the relatively low levels seen in 95Pt5Co, these two alloys were chosen for the present report on microstructural changes brought about by the HIP process. **Figure 5** demonstrates significant porosity levels in the as-cast state of 95Pt5Ru. The pores in this alloy are interdendritic microshrinkage pores; such pores form during the spontaneous solidification of the alloy that occurs so rapidly that continued feeding is not possible. The HIP process has successfully closed these microshrinkage pores, such that the microstructure is completely dense after HIPing.

Another important finding is that grain size is not negatively affected by the HIP process (**Figure 6**). A simple heat treatment to the same thermal parameters as the HIP processing (without the use of pressure) is neither capable of fully closing the pores from the as-cast condition, nor maintaining grain size (**Figure 7**). While the amount and the size of pores are clearly reduced, grains are growing substantially during heat treatment. Thus, any beneficial effect of porosity reduction is compromised by grain growth. Based on this result, it would appear that the pressure used in the HIP process has the added benefit of retarding grain growth. **Figure 8** demonstrates the comparative grain sizes of 95Pt5Ru in the as-cast, HIPed and heat-treated conditions.

The casting sample of 95Pt5Co shows no visible macroscopic or microscopic porosity in the as-cast condition (**Figure 9**). However, compared to 95Pt5Ru the grains are extremely large. Their size and shape indicates a relatively slow solidification process

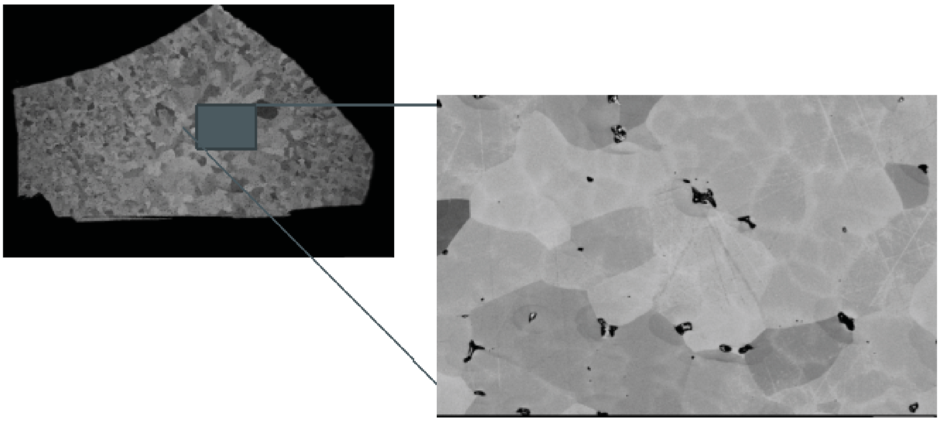

Fig. 5. 95Pt5Ru as-cast showing numerous interdentric microshrinkage pores present in the as-cast condition and uneven grain size distribution with coarse columnar grains at the surface

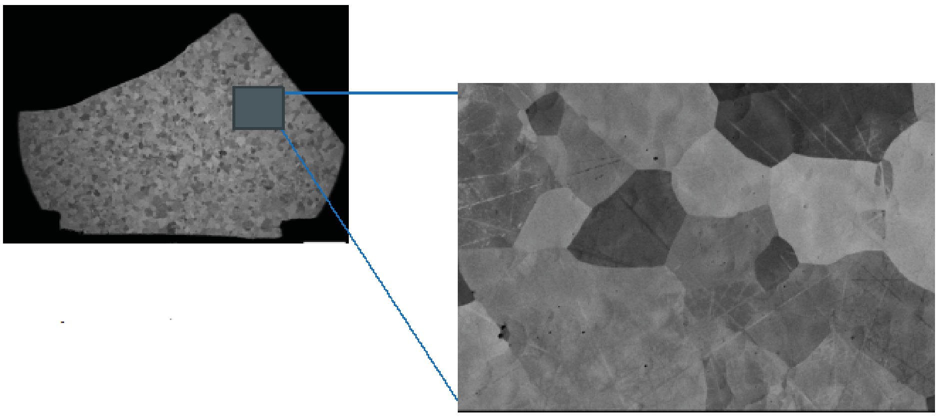

Fig. 6. 95Pt5Ru HIP which has dense and pore-free microstructure and even grain size distribution. HIP pressure appears to retard grain growth

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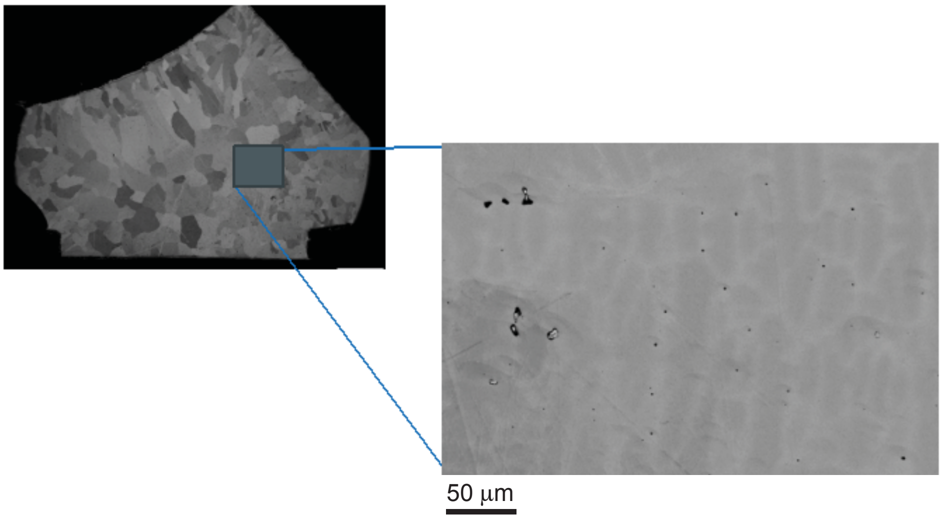

Fig. 7. 95Pt5Ru heat treatment using same thermal curve as HIP, showing reduction of microshrinkage porosity and heavy grain coarsening during thermal processing

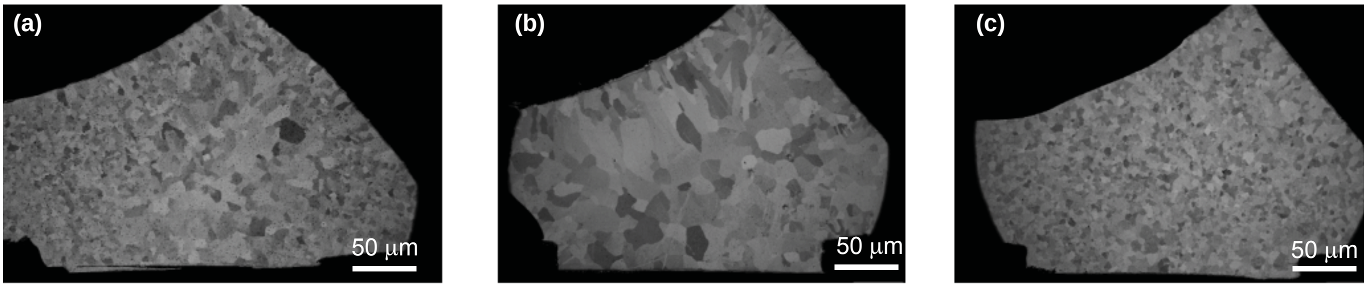

Fig. 8. Comparative microstructures of 95Pt5Ru: (a) as-cast; (b) heat treated; (c) HIPed

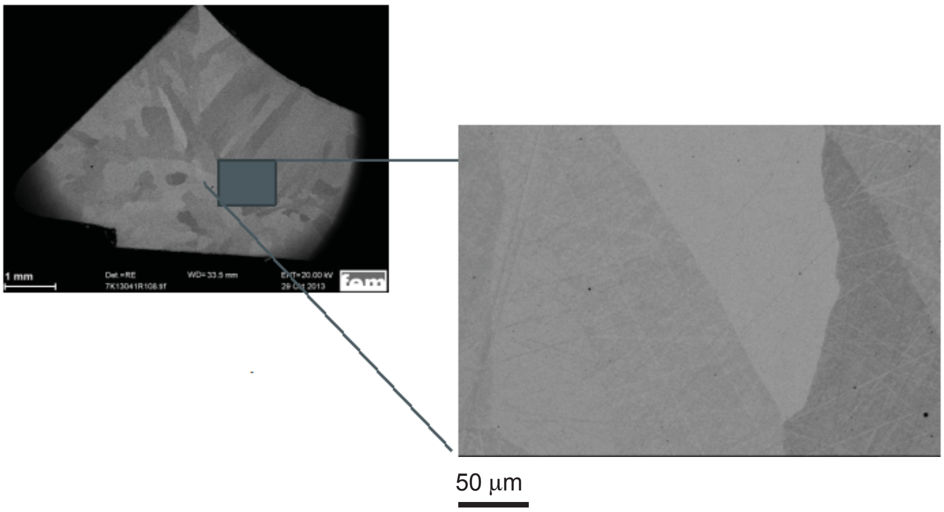

Fig. 9. 95Pt5Co as-cast showing very large columnar grains growing from the surface during solidification and no macroscopic or microscopic porosity in as-cast condition

where a few grains were nucleated at the surface of the part, which then grew into the centre. As a consequence, there was sufficient time for feeding and the microstructure is free of pores. Therefore, during HIPing few changes of the microstructure occurred in the 95Pt5Co (**Figure 10**). This is not to say that HIP does not provide any benefit to 95Pt5Co castings. The previous research on larger samples demonstrated a tendency of this alloy to form large gas pores and centreline shrinkage porosity that were either eliminated or reduced in size by the HIP process.

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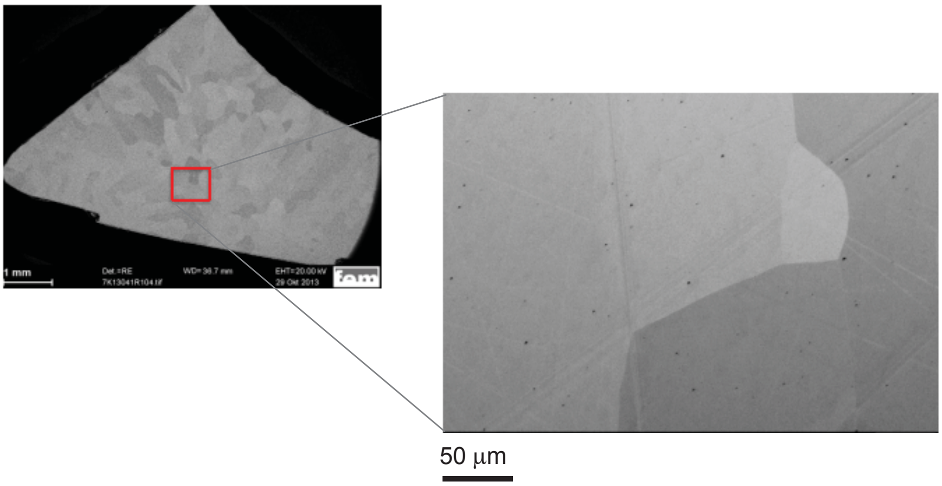

Fig. 10. 95Pt5Co HIP showing no significant change of microstructure during HIPing

Alloy Density

Density of the test samples was measured using the Archimedes' Principle (3) to determine levels of densification achieved through the HIP process. Although the density of the as-cast samples was already very high, HIP increased the levels to near 100%. This result is impressive and effectively puts castings on a par with wrought material. As can be seen in **Table III**, HIP most effectively increased density in 95Pt5Ru and 90Pt10 Rh and was slightly less effective for 90Pt10Ir, which we can see already starts out with higher as-cast density. This result correlates well with the generally lower levels of visible porosity seen in 90Pt10Ir cross-sections from the 2011 study (1). Although 95Pt5Co was not tested for density, one would expect similar findings as in the case of 90Pt10Ir due to the lower levels of porosity in the as-cast state.

Certain defect types either do not respond to HIP or have a lower densification response. A key limitation of the process is that only porosity that is fully subsurface will collapse; if pores are open to the surface of the casting in any way, they will not respond to HIP. This effect can be seen in the shrinkage porosity (**Figure 11(a)**). Another limitation of HIP is seen in gas pores. Pores created by gas are less responsive to HIP than shrinkage pores due to the pressure they contain. Rather than being eliminated, the pores are typically reduced in size by HIP as can be seen in the cross-section (**Figure 11(b)**).

Alloy Homogeneity and its Effects on Segregation

Another aspect of the present study was determining whether there had been any change in segregation

Table III Alloy Density Results

Alloy	Condition	Density, g cm^{-3}	Relative density
95Pt5Ru	As-cast	20.32	98.4%
95Pt5Ru	HIPed	20.62	99.9%
90Pt10Ir	As-cast	21.39	99.5%
90Pt10Ir	HIPed	21.48	99.9%
90Pt10Rh	As-cast	19.58	98.2%
90Pt10Rh	HIPed	19.89	99.7%

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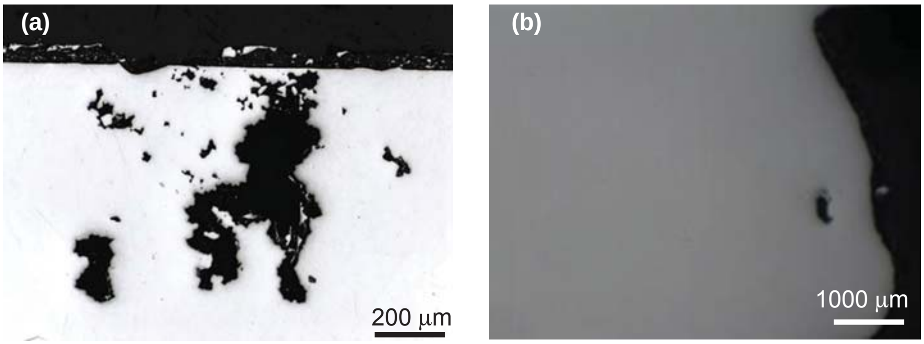

Fig. 11. (a) Surface connected shrinkage porosity in 95Pt5Ru; (b) sectioned Pt90Ir10 gas pore after HIP

of the alloying elements during high temperature heat treatment or HIP. By contrasting EDX mapping of 95Pt5Ru in the as-cast, heat treated, and HIPed conditions, we found that Ru segregated to the primary dendrites during solidification in a similar manner for all three conditions. Thus, neither heat treatment nor HIP changed the segregation of Ru. As can be seen in the comparative images in **Figure 12**, after HIP the dendrites have coarsened, but the microstructure is not negatively affected because the dendrites have arms that can coarsen without changing the overall size of the dendrite (**Figure 12(c)**).

Tensile Testing

A literature search for mechanical properties data on cast platinum alloys showed that there are few publications in this area, with the exception of microhardness values that are frequently cited by jewellery industry sources. A publication from 1978 by Ainsley and Rushforth (4) was likely one of the earliest to look at tensile properties from actual castings *versus* the more commonly cited mill product values. These authors published values on nearly a dozen different platinum casting alloys including two that are also covered in the present testing. It is notable that the values they published for the same alloys tested here were appreciably lower in the as-cast state. Although it is not known why this was the case, a plausible explanation might be the difficulty of obtaining high quality cast test bars with the technologies available in 1978.

This relative scarcity of hard data is not so surprising given that sophisticated platinum casting is a relatively new development. It was not until the mid-1990s that induction machines capable of handling platinum's high temperature requirements became mainstream. Prior to that, small-scale oxyhydrogen torch melting was the only method available and inconsistent quality coupled with low pour weight capacity prevented investment casting from becoming a mainstream industrial process for platinum. All of that has of course changed and platinum based alloys are now routinely investment cast with induction melting methods on a global basis.

While as-cast tensile properties of platinum alloys are of keen interest in their own right, an additional motivation to perform this testing was as a means to compare the strength characteristics of as-cast *versus* HIPed platinum alloys. In theory, the higher density

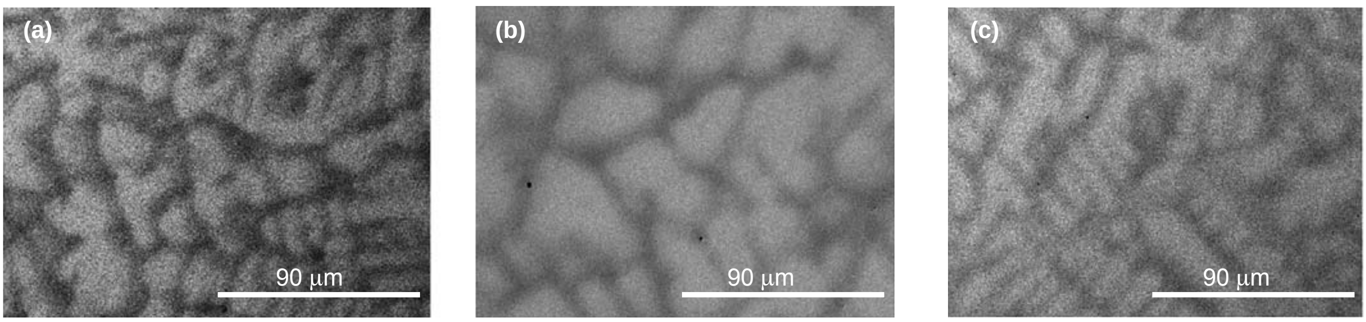

Fig. 12. (a) Pt95Ru5 as-cast; (b) Pt95Ru5 heat treated; (c) Pt95Ru5 HIPed

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of HIPed product would show increased values for a number of tensile properties. **Table IV** outlines the testing plan that was followed to produce the data, followed by **Figure 13** depicting the test bar geometry used for the tensile tests. Tensile testing was carried out in accordance with international standards (5).

The results in **Table V** report values for yield strength (YS), ultimate tensile strength (UTS), elongation (ε) and reduction of area (ROA). Yield strength describes stress levels above which plastic deformation occurs and will generally increase with decreasing grain size. Following yielding, the material work hardens by the generation of dislocations. As a consequence, the required stress for further deformation increases until the ultimate tensile strength is reached. In metals, the UTS values will generally correlate with Vickers hardness values.

At strains above UTS, which marks the maximum of the stress-strain curve (**Figure 14**), the cross-section is locally reduced through necking of the sample. Further deformation is localised in the necking region and as a consequence the required stress for further deformation is continually decreasing until failure occurs. The total elongation (ε) indicates how much plastic deformation the material can withstand. Pores in the material will significantly reduce the elongation because they act as stress concentration sites. The effect of pores is even more pronounced on the reduction of area, which indicates how much necking occurs until the sample finally fails.

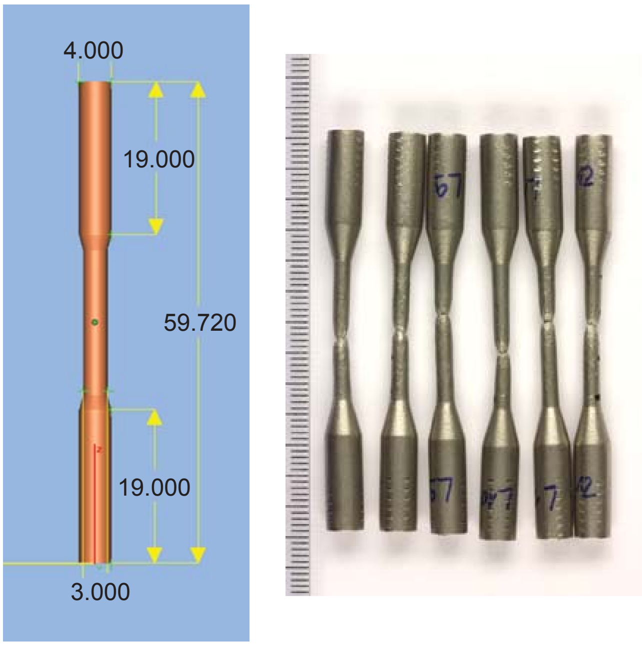

Fig. 13. Test bar geometry: simple design, heavy molten feed to gauge area with double end gates, directional solidification from interior of bar towards outer heavy sections optimizes gauge area (units in mm)

While UTS or hardness are clearly important properties to measure, they are not necessarily the most critical properties to predict failure in a broad number of applications. When it comes to fatigue life, elongation and reduction of area are generally viewed as being more important. Specifically, in cases where

Table IV Casting Specifications for Tensile Bars

Alloy	Pour temp., ºC	Flask temp., ºC	Number of test bars	Casting condition
95Pt5Ru	1870	850	12	6 As-cast; 6 HIPed
90Pt10Ir	1870	850	8	4 As-cast; 4 HIPed
90Pt10Rh	1960	850	8	4 As-cast; 4 HIPed
95Pt5Co	1850	850	8	4 As-cast; 4 HIPed

Notes to Table IV
(a) Total bars: 36; minimum tests required: 18
(b) Test bar locations in ‘upper’ and ‘lower’ centrifuge orientation
(c) All waxes turned on lathe for dimensional precision
(d) All bars identically wax assembled with double end gates
(e) All bars cooled identically
(f) All bars HIPed to the same parameters

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Table V Tensile Properties

Alloy composition	Condition	Yield strength, MPa	Ultimate tensile strength, MPa	Elongation, %	Reduction of area,%	Change in reduction of area,%
95Pt5Ru	As-cast	225	412	30	55	–
95Pt5Ru	HIPed	236	420	39	87	+32
90Pt10Ir	As-cast	219	353	33	90	–
90Pt10Ir	HIPed	226	358	36	87	–3
90Pt10Rh	As-cast	140	330	37	64	–
90Pt10Rh	HIPed	144	333	43	89	+25
95Pt5Co	As-cast	220	452	36	76	–
95Pt5Co	HIPed	189	449	38	82	+6

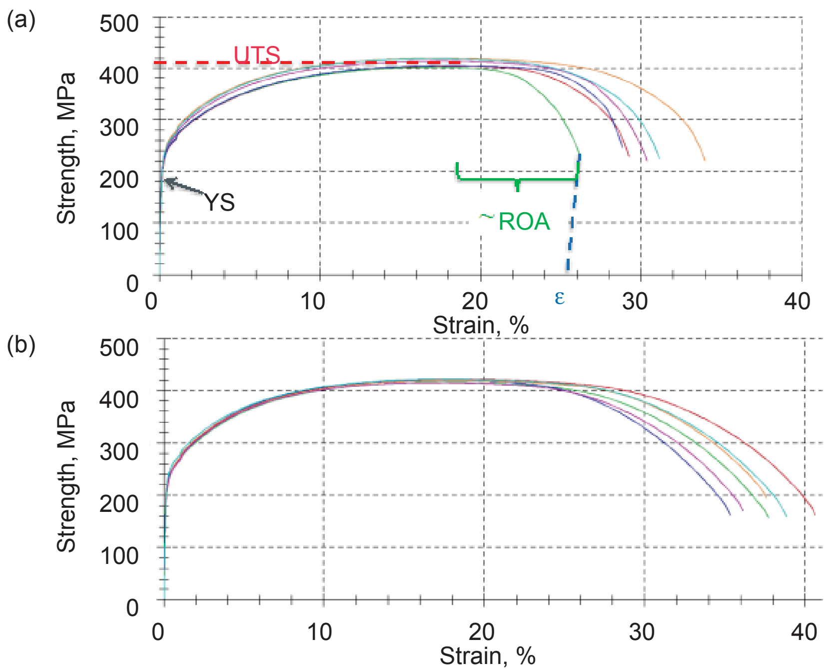

Fig. 14. UTS scatter of 95Pt5Ru: (a) as-cast; (b) HIPed

subsequent cold working of the material is involved, an increased ability to bend before cracking is of paramount importance.

The HIP treatment affects the mechanical properties of the four alloys in a different way. For all alloys the effect on YS and UTS is rather low. For 90Pt10Ir and 95Pt5Co there is little effect on elongation and ROA. However, for 95Pt5Ru and 90Pt10Rh a significant increase in elongation and ROA is found through HIPing. These results correlate well with the porosity levels of the different alloys, and are a clear indication that reduction of porosity increases ductility in the alloys.

Another interesting observation came from an analysis of UTS scatter in the sample population. The graphs in **Figure 14** demonstrate the difference in spread between the as-cast and HIPed groups. The HIPed bars exhibit a very tight distribution, whereas the

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as-cast bars are more scattered. This result correlates well with observations of lower porosity levels together with a more homogeneous grain size and structure in the HIPed samples.

As stated above, reduction of area values posted the most impressive gains in the HIPed product. This property is of particular interest in the jewellery industry given the substantial amount of bending and forming that is inherent in stone setting, engraving, sizing and myriad bench operations. Reduction of area indicates a material's ductility and is crucial to successful performance in many of these operations. **Figures 15(a)** and **15(b)** demonstrate a profound visual difference in ductility between the test bar fractures in the as-cast and HIPed 95Pt5Ru.

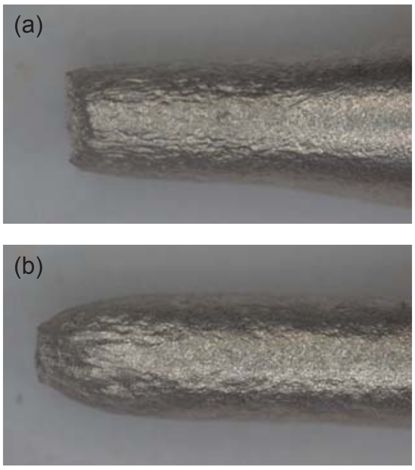

Fig. 15. (a) 95Pt5Ru as-cast 55% ROA; (b) 95Pt5Ru HIPed 87% ROA

Hardness Testing

Table VI reports Vickers hardness values (6) for three of the tested alloys. With the possible exception of 95Pt5Ru, all alloys report values that are so close in the before and after HIP conditions that any difference is seen as essentially inconsequential. Even the 95Pt5Ru that shows a 12-point spread is not considered enough to be characterised as an appreciably harder material by performance. Thus we can conclude that hardness is not significantly impacted by HIP on the platinum-based alloys we tested.

Table VI Vickers Microhardness Results

	Vickers Hardness HV_1[a]		
Alloy	As-cast	HIPed	Heat treated
90Pt10Ir	113	111	123
90Pt10Rh	89	89	n/a
95Pt10Ru	113	125	128
95Pt5Co	126	122	n/a

[a] Error: ± 3 HV_1

Conclusions

The most significant impact of HIP on platinum-based alloys is a reduction in porosity. Reduced levels of porosity have several associated benefits, including a marked increase in ductility in the majority of the alloys tested without sacrificing strength. Of the tensile properties tested, the most impressive response was found in the values for ROA, a key indicator of an alloy's ductility.

Another meaningful result demonstrated here was HIP's effect on grain structure and size. Although further testing is needed to fully characterise this aspect, our initial research confirms a more uniform grain size and structure in the HIPed samples without any increases in grain size, at least for the alloy 95Pt5Ru.

Findings also confirm that the response to HIP is strongly impacted by the alloy's composition. 95Pt5Ru benefits the most due to its higher levels of porosity present in the as-cast condition, and 95Pt5Co having lower porosity benefits the least.

Further work is recommended to more closely assess the impact of qualitative changes in the HIPed product on manufacturing operations. Empirical evidence strongly suggests greater ease in post-cast operations due to the elimination of sub-surface micro-porosity and a generally more consistent metallurgical condition, including uniformity of grains. In addition, the increased ductility of HIPed platinum alloys should, in theory, result in a lower number of failures during metal bending and forming operations.

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References

1. T. Fryé and J. Fischer-Bühner, 'Platinum Alloys in the 21st Century: A Comparative Study', in "The Santa Fe Symposium on Jewelry Manufacturing Technology 2011", ed. E. Bell, Proceedings of the 25th Symposium in Albuquerque, New Mexico, 15th–18th May, 2011, Met-Chem Research Inc, Albuquerque, New Mexico, USA, 2011, pp. 201–230
2. "Elements of Metallurgy and Engineering Alloys", ed. F. C. Campbell, ASM International, Ohio, USA, 2008, p. 265
3. "Standard Test Method for Density, Oil Content, and Interconnected Porosity of Sintered Metal Structural Parts and Oil-Impregnated Bearings", (Withdrawn 2009), ASTM Standard B328-96(2003)e1, ASTM International, West Conshohocken, Pennsylvania, USA, 2003
4. G. Ainsley, A. A. Bourne and R. W. E. Rushforth, *Platinum Metals Rev.*,1978, **22**, (3), 78
5. "Metallic Materials – Tensile Testing – Part 1: Method of Test at Room Temperature", DIN EN ISO 6892-1: 2009-12, Deutsches Institut für Normung e.V., Berlin, Germany, 2009
6. "Metallic Materials – Vickers Hardness Test – Part 1: Test Method", DIN EN ISO 6507-1:2006-03, Deutsches Institut für Normung e.V., Berlin, Germany, 2006

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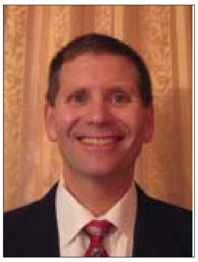
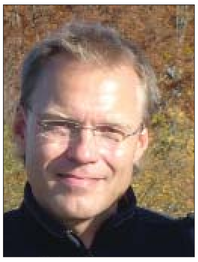


Joe Strauss has a PhD in Materials Engineering from Rensselaer Polytechnic Institute, USA. He has over 30 years of experience in developing atomisation and powder metallurgy technologies for non-traditional materials including precious metals for jewellery, dental, electronic and medical applications. His work includes design and fabrication of atomisation systems, research and development in powder metallurgy and engineering troubleshooting for manufacturing processes.



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