https://doi.org/10.1595/205651322X16390711562364

Johnson Matthey Technol. Rev., 2022, **66**, (4), 418–434

JOHNSON MATTHEY
TECHNOLOGY REVIEW

technology.matthey.com

The Evolution of Platinum Jewellery Alloys: From the 1920s to the 2020s

Developments in new alloys and techniques

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PEER REVIEWED

Received 6th October 2021; Revised 8th December 2021; Accepted 9th December 2021; Online 9th December 2021

Platinum has only been known to Europe since the 16th century. This was impure platinum, found as grains of native metal in alluvial deposits and comprising mainly platinum alloyed with the other five platinum group metals. They were exploited by pre-Colombian native populations of Ecuador and Colombia. In more recent times, the use of platinum in jewellery dates from the late 19th or early 20th centuries, often as a basis for diamond (and other precious gemstone) jewellery. Early jewellery alloys tended to be based on the existing industrial alloys and comparatively little development of specific jewellery alloys was carried out. Its acceptance as a hallmarkable jewellery metal came in 1975 when, with wider availability of the metal, platinum was promoted as a high-value jewellery metal. Platinum jewellery started to grow in popularity, mainly at 950 and 900 fineness qualities. Since that time there has been alloy development specifically for jewellery application and tailored to the requirements of different manufacturing technologies. This review examines the evolution of platinum jewellery alloys over the past century against the challenges presented in developing improved alloys for jewellery application. There has been a substantial increase in alloy development over the past 30 years, particularly focused on improved investment (lost wax) casting alloys as well as better mechanical properties.

1. Introduction

Platinum has been known to Europe since the 16th century, beginning with rumours of the existence of a white metal, known as *platina*, in Central and South America that could not be melted (1). This impure platinum, found as grains of native metal in alluvial deposits, is often associated with native gold. Such grains are mainly platinum alloyed with the other five platinum group metals (pgms): palladium, rhodium, ruthenium, osmium and iridium, and were exploited by pre-Colombian native populations of Ecuador and Colombia in north-western South America. Analysis of ancient trinkets indicates that iron and copper were also present as impurities (1).

Since that time, global interest in platinum jewellery remained low until the technology to separate the pgms was developed and its metallurgy was researched and understood. The interest in using platinum as a jewellery metal developed from this time but its popularity really grew in the mid-to-late 20th century. This has been followed by considerable alloy development suited to jewellery application and the manufacturing processes in use. This paper reviews the evolution of conventional platinum jewellery alloys over the past 100 years or so. A few comments on other alloys are made later in the discussion section. Unless otherwise noted, all compositions in this paper are in weight percent.

It is worth noting that the main interest in platinum and its alloys over the past century (and longer) has been for industrial applications (1).

Typical uses include catalysts, dental alloys, electrical contacts, crucibles for melting glass and equipment for glass fibre production, spark plug electrodes, thermocouples for temperature measurement, biomedical devices and coatings for glass processing and jet engines. Many of these are well described in various articles in the archive of *Platinum Metals Review* and *Johnson Matthey Technology Review*. Platinum is a precious and rare metal that is very ductile, tough, corrosion resistant and chemically unreactive. It has a lustrous silver-white colour, features that make it attractive for jewellery application. It has a high density and a high melting point, with a low thermal conductivity and is relatively expensive.

2. Jewellery Alloys: The 1920s to the 1990s

The popular use of platinum in jewellery dates from the late 19th to early 20th centuries, often as a basis for diamond (and other precious gems) jewellery. Smith, in his book published in 1933 (2), noted its use in jewellery at 99.5% platinum purity (995 fineness) with small additions of alloying metals to harden it, including iridium, rhodium, ruthenium, gold, silver and copper. He also noted that the platinum standard (in the UK) was 950 fineness (i.e. parts per thousand) which was finding general acceptance. The term 'platinum' was deemed to include iridium. He further noted that much of the platinum used in jewellery was alloyed with copper to improve hardness and colour.

The use of platinum in jewellery was restricted in the Second World War as it was considered a strategic industrial metal with limited availability, which led to the development of white gold alloys as an alternative for jewellery. The early platinum jewellery alloys tended to be based on existing industrial alloys and comparatively little development of specific jewellery alloys was carried out. These tended to be 90–95% platinum alloyed with other pgms, typically iridium. These alloys have high melting temperatures, making manufacturing of jewellery, particularly investment (lost wax) casting, difficult and challenging for the jeweller used to gold and silver. Raykhtsaum has reviewed selected literature on platinum alloy systems used in industry and for jewellery (**Table I**) with a focus on their metallurgy and properties (3). There is quite a range of mechanical properties possible but he notes that the legal requirements on minimum platinum content for jewellery limits the alloy range and prohibits the utilisation of enhanced mechanical properties of many alloys outside this range.

A further issue with the use of platinum alloys in jewellery had been the lack of accurate analysis techniques. This meant that its acceptance as a hallmarkable jewellery metal in the UK came much later, in 1975 (4, 5). From this time, with its now much wider availability, platinum was promoted by the platinum producers as a rare, high-value jewellery metal. Platinum jewellery grew in popularity, mainly at 950 and 900 fineness qualities, in Japan, Europe and the USA, although some growth in demand began earlier in Japan in the 1960s (for historical reasons linked to the ban on the import of gold until 1973). Platinum Guild International was formed by the producers in 1975 to promote platinum usage in jewellery and its marketing, coupled with growth in usage, led to some alloy development, including the 950 fineness platinum-5% cobalt alloy for investment casting (6) and the use of gallium additions to produce heat treatable alloys with higher strength and hardness (7), as Normandeau has reported (8, 9). For example, one European platinum producer

Table I Platinum Alloy Systems Reviewed by Raykhtsaum (3)

Alloy System	Comments	Ternary additions
Pt-Pd	Soft alloys	Ru increases hardness
Pt-Ir	Harder and stronger than Pt-Pd. Commonly used in jewellery at 5% and 10% Ir	Rh enhances mechanical properties
Pt-Rh	Soft, ductile alloys	Ru enhances strength but loss of ductility
Pt-Ru	Harder and stronger. Commonly used in jewellery	–
Pt-Au	Miscibility gap and spinodal decomposition a feature. Au is a very effective hardener but ductility drops due to grain growth during solution treatment	Rh enhances hardness, strength and ductility. Alloys are hardenable
Pt-W, Pt-Co	Most studied of Pt-base metal systems	–
Pt-Cu, Pt-Co, Pt-Ni, Pt-Ga	Are all age-hardenable systems	–

listed only four alloys for jewellery application in their internal catalogue dating to the late 1980s, all at 950 fineness: platinum-copper, platinum-cobalt, platinum-ruthenium and platinum-gallium-indium. The copper alloy was listed as a general-purpose alloy (i.e. suitable for wrought fabrication and casting applications) and the cobalt alloy was listed as suitable for investment casting. Another European producer listed only three alloys at 950 fineness: Pt-5Cu, Pt-5Co/Ni and Pt-5Ru.

The work to develop the 950-fineness platinum-cobalt alloy for casting was described by Ainsley, Bourne and Knapton (6) in 1978; they actually developed it as a platinum-4.5% cobalt alloy. It was aimed originally at meeting the needs of the Japanese market, but soon became popular in Europe too. Unlike several of the existing platinum alloys, it has a lower melting range which puts less thermal strain on the mould refractories and reduces the likelihood of metal-mould reaction. It also has a moderate hardness of about HV135, better than most of the other 950 fineness alloys of that era.

Huckle of Johnson Matthey, UK, reported on the development of platinum alloys to overcome production problems at the 1996 Santa Fe Symposium (10, 11). He noted that platinum and its alloys had some different characteristics compared to gold and silver, notably weight, hardness and thermal conductivity and that its alloys have a high density, as well as high melting points. Its high surface resistance leads to clogging (galling) and high wear of saw blades, files and machine tools. He noted that, in Japan, platinum-palladium alloys were in common use, particularly Pt-10Pd, whereas in Europe Pt-5Cu was preferred. It is not a good casting alloy, whereas for casting applications Pt-5Co was finding success. In the USA, he noted that Pt-10Ir was commonly in use as an all-purpose alloy (i.e. suitable for wrought fabrication and casting) and that Pt-5Ru was used where a hard, good machining alloy is needed. He also noted that Pt-5Co was finding growing use for casting applications in the USA.

Maerz of Platinum Guild International, USA, also reviewed platinum jewellery alloys at the 1999 Santa Fe Symposium (12). This built on the information provided by Huckle. He summed up the alloys widely available and their application in jewellery at that time with some comment on the new alloys being introduced.

In this context, Maerz and Huckle noted that it is important to recognise the different marking standards for jewellery of various countries at that time. Maerz noted that European countries generally allowed only 950 fineness alloys, with some allowing no negative tolerance (Austria, Ireland, Sweden, Norway, Finland, the UK and Switzerland), some allowing a small negative tolerance (Denmark, Portugal and Italy) and others allowing iridium content to be counted as platinum within the 950 standard (Belgium, France, Italy, Greece, The Netherlands and Spain). In Germany, he noted that several fineness standards and alloys were allowed (**Table II**).

In the USA, Maerz noted that the standard for jewellery to be marked as platinum was 950 fineness. The minimum amount of platinum allowed was 500 parts per thousand, with the rest of the alloy being pgms, in total comprising 950 parts per thousand with a zero tolerance. He also noted that 950, 900 and 850 fineness standards were allowed in Japan. Regarding actual alloy compositions, he noted that each alloy was made for specific manufacturing functions. Some alloys were preferred for tubing or machining and others for casting, for example; and there were differences in preference in different countries. **Table III** lists the alloys in common (or growing) usage around the world with their function and countries of major use. He also listed separately a number of alloys that are specific to Japan and these are included in **Table III**.

Maerz's list did not record the platinum-5% copper alloy (except for its use in Japan) which has been mentioned above as an alloy commonly used in Europe. Maerz did note that, in the USA, the most common alloys in use were 950 platinum with 5% cobalt or ruthenium and 900 platinum with 10% iridium. However, in an updated later version of his paper (14), the Pt-5Cu alloy was included in the general alloy list.

Table II Platinum Alloys Allowed in Germany (12)

Fineness Standard[a]	Alloy
999	Pt
960	Pt-Cu
950	Pt-Pd
	Pt-In-Ga
	Pt-W
	Pt-Co
	Pt-Ru
900	Pt-Ir
800	Pt-Ir

[a]Fineness = parts per thousand

Table III Platinum Jewellery Alloys Around the World in 1999 (12)

Fineness standard	Alloy	Hardness, HV	Application	Country
950	Pt-Ir	80	All purpose[a], casting; soft alloy	Germany, Japan, USA
	Pt-Co	135	Casting (slightly magnetic)	Germany, Europe, Hong Kong, Japan, USA
	Pt-Co-Cu	120	Casting, malleable (non-magnetic)	USA
	Pt-Cu	120	General purpose[a] (96Pt-4Cu)	Germany, Europe, Hong Kong
	Pt-Pd	60	Soft alloy; fine detailed casting	Japan, Hong Kong, Europe
	Pt-Pd-Ru		Chainmaking (4Pd-1Ru)	Japan
	Pt-Au	90; aged[b] 300	All purpose, soft but heat treatable	General use worldwide
	Pt-Ru	130	Tubing for wedding bands	Europe, Hong Kong, USA
	Pt-W	135	Spring alloy; heat treatable	Germany, Europe
	Pt-Ga-In	225	Heat treatable (3Ga-1.5In); hard alloy; machining tube, springs	General use worldwide
	'HTA'[c]	175–185; aged 340-360	Heat treatable (4.8(Ga+In+Cu))	General use worldwide
	S + 1[d]	135–145; aged 252	Contain Ga; heat treatable	General use worldwide
	S + 2	170–200; aged 306	Contain Ga; heat treatable	General use worldwide
900	Pt-Ir	110	All purpose; widely used in USA	USA, Japan, Germany
	Pt-Co-Pd	150	Hard casting alloy (3Co-7Pd)	Japan only
	Pt-Pd	80	All purpose; greyish colour; needs Rh plating; chainmaking	Japan, Hong Kong
	Pt-Pd-Cu	110	3–5% Cu improves hardness and workability	Asia
	Pt-Au	135	All purpose	Europe, Japan, South Africa
	Pt-Pd-Au		Similar but softer than 900 Pt-Au	–
	Pt-W	350	Hard alloy, findings	UK
	Pt-Pd-W	150	All purpose	Asia
850	Pt-Ir	160	Findings	Japan
	Pt-Pd	90	Soft; chainmaking	Japan, Hong Kong
	Pt-W	251	Spring alloy; heat treatable	UK
	Pt-Pd-Co	150	Harder Pt-Pd alloy for Asia	Japan
	Pt-Pd-Cu		Chainmaking (8Pd-7Cu or 10Pd-5Cu)	Japan
800	Pt-Ir	200	Hard alloy, mesh and chainmaking	Germany only

[a]All purpose/general purpose = suitable for wrought fabrication and casting
[b]Aged = precipitation hardened by heat treatment
[c]HTA = 950 platinum-4.8%(Ga-In-Cu) alloy (8)
[d]S = 'S' alloys developed by Steven Kretchmer, USA (13)

These reviews do not include the alloys in use in the former Union of Soviet Socialist Republics (USSR). In his book published in 1984, Savitskii (15) noted only two 950 fineness alloys were in use: Pt-5Ir in Russia and Pt-4.5Pd-0.5Ir in the former East Germany (GDR).

3. Technical Aspects of Alloys: The 1920s to the 1990s

From the list of alloys summarised in **Table III**, it is evident that at 950 and 900 fineness qualities, there is a broad range of alloys with varying mechanical properties available to the jeweller, each suited to various manufacturing techniques. All have a good white colour, although some, such as Pt-10Pd alloy, may benefit from rhodium plating to give a brighter, whiter colour. The main differences lie in their hardness (or strength) and melting ranges.

Battaini examined the microstructure of several platinum alloys (16, 17) and noted that many alloys are single phase, as one might expect from examination of their phase diagrams, particularly at 950 and 900 fineness qualities. Some alloy systems, however, show large areas of miscibility gaps at low temperatures, for example platinum-gold and platinum-copper systems, and this raises the possibility of age-hardening alloys by heat treatment, whereby a fine precipitate of a second phase within the matrix grains is obtained by a low-temperature annealing treatment. Platinum-5% gold is an example here (**Figure 1(a)**) where an aged hardness of HV300 can be attained, leading to better scratch and wear resistance. Its use in as-cast 950 platinum-gold rings has not been observed (18, 19), suggesting it is a treatment not in common use. Platinum-cobalt (**Figure 1(b)**) forms an ordered intermetallic compound, Pt_3Co, that could, perhaps, just enable some hardening at 950 fineness (it is also magnetic). The use of gallium also allows age hardening, as is evident from the platinum-gallium phase diagram (**Figure 2**), as well as lowering melting temperature ranges. Its use forms the basis of several heat treatable alloys as noted earlier and listed in **Table III**. Indium has a similar effect in lowering the melting temperature range and is being used in several newer alloys, as described later.

The development of age-hardenable alloys using gallium additions stems from the late 1970s. The work of Bourne and Knapton led to the development of the 950 platinum-3% gallium-1.5% indium alloy (7). In their patent, they also referred to platinum-gallium-gold alloys as an option, with the use of yttrium additions of about 0.1% as a deoxidiser. The alloy Pt-3Ga-2Au was claimed to have a high hardness of HV200. Such gold-bearing alloys were said to cast well. Interestingly, while platinum-gallium-gold alloys like those in the invention were said to be suitable for springs, there was no mention in the patent of heat treatments to age harden the gallium-containing alloys.

This early work subsequently led to the development of other gallium-containing alloys that were claimed to be heat treatable. Normandeau and Ueno (Imperial Smelting, Canada) reported

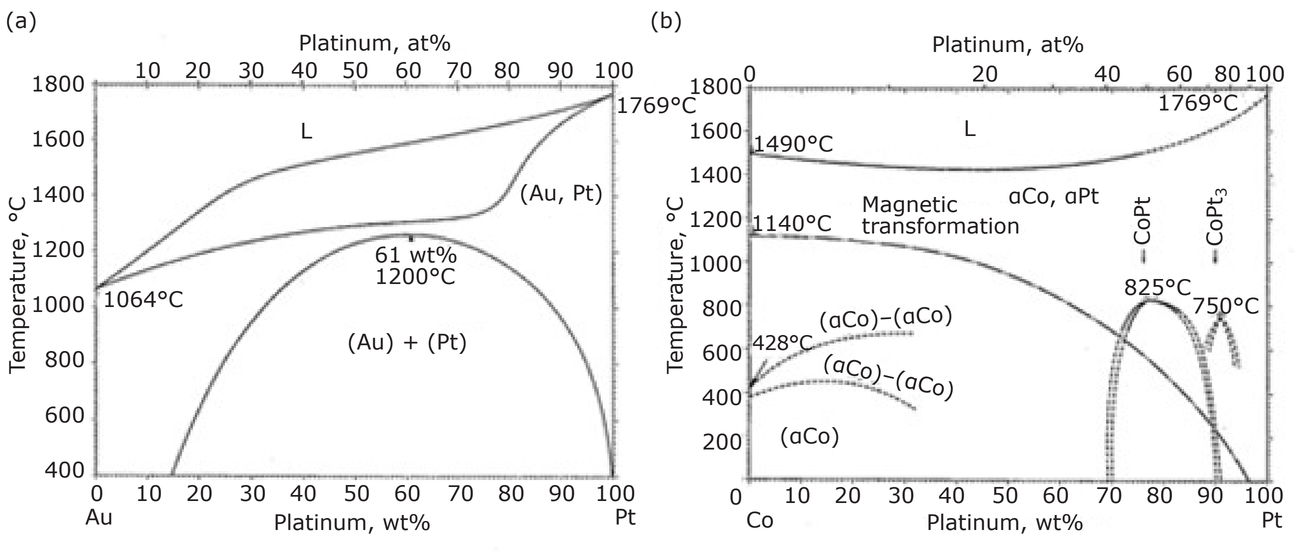

Fig. 1. Phase diagrams: (a) platinum–gold; (b) platinum–cobalt

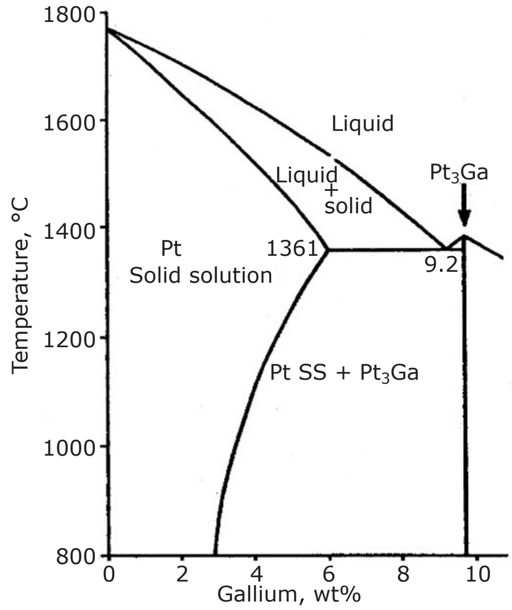

Fig. 2. Platinum–gallium partial phase diagram

that platinum alloyed with tungsten, gold, gallium, indium or copper was age-hardenable by heat treatment. They described research to develop their 'HTA' alloy, which is a 950 platinum-4.8% (gallium-indium-copper) alloy which can be age-hardened to HV340–360 and up to HV420–430 if aged in the cold-worked condition (8). Kretchmer also developed gallium-containing alloys (20, 21) including 950 platinum-gallium-palladium that can be age-hardened to HV320. A further patent described the age-hardening treatment of platinum-gallium-palladium alloys (20, 21) that involves solution treatment at 982°C or higher followed by an ageing treatment at 593–649°C. This work stemmed from research reported in 1998 (13).

Clearly, some alloys are quite soft (hardness lies in range HV50–100), some have a moderate hardness (HV100–150) and others are quite hard (HV 150–350). The higher values are usually when in the age-hardened condition. In a recent study of customer complaints by the present author (18, 19), it was noted that use of soft alloys is a significant factor in platinum (and other) jewellery becoming deformed in shape and badly scratched when worn by consumers, particularly in as-cast gem-set rings and wedding bands.

Work around the turn of the 21st century and summarised in recent reviews (22, 23) demonstrated that microalloying of pure platinum and its alloys with very small additions of calcium and/or rare earth metals such as cerium, samarium and gadolinium, typically up to about 0.3%, can increase hardness substantially but such microalloys do not appear to have been significantly commercialised by the jewellery industry, probably because they are not easily cast or recyclable (melting causes the alloying additions to oxidise away).

The melting point of pure platinum is 1769°C, considerably higher than gold (1064°C) and silver (961°C). Its alloys tend to have similarly high melting temperature ranges, as shown in **Table IV**, although the gallium-containing alloys do have a significantly lower melting temperature range. Thus, melting and casting platinum alloys requires good furnace equipment capable of attaining melt temperatures some 100°C above the liquidus temperature of the alloy for investment casting. Induction melting is preferred. Melting by gas torch is not easy, although a propane-oxygen or hydrogen-oxygen torch can be used by bench jewellers. However, in general, working of platinum alloys is not a problem, although polishing requires skill and effort to obtain a good quality polish. Machining of platinum also requires skill to obtain a good smooth finish, requiring special tool materials and different tool geometries (25), as platinum tends to gall (adhere) on the tool. The low thermal diffusivity of platinum alloys makes welding easier, particularly laser welding (26, 27) compared to gold and silver alloys.

The major manufacturing problem has been with investment casting. The high melting and casting temperatures require use of special phosphate-bonded investment mould materials (28) and the poor melt fluidity requires use of centrifugal casting machines (29) to obtain good mould fill rather than the modern gravity machines commonly used for gold and silver. The new generation of tilt casting machines are also suitable. The chief problem with platinum casting is getting defect-free castings (10, 29–31). There have been several investigations on the relative merits of different alloys (6, 31–37), looking particularly at surface quality, form-filling and gas and shrinkage porosity. An evaluation of platinum-5% cobalt alloy was reported by Todd *et al.* at Stuller Settings Inc, USA, in 1998 (31), comparing its casting behaviour with platinum-5% ruthenium and platinum-10% iridium alloys. They found that the cobalt alloy was superior with reduced porosity and smoother surfaces. The general findings from all these studies show the Pt-5Co alloy to be the best of current alloys but still not ideal.

Table IV Physical Properties of Platinum Alloys[a]

Fineness standard	Alloy	Liquidus–solidus temperature, °C	Density, g cm^{-3}
950	Pt-Ir	1790–1780	21.5
	Pt-Co	1765–1750	20.8
	Pt-Co-Cu	1760–1750	20.1
	Pt-Cu	1745–1725	20.8
	Pt-Pd	1765–1755	21.0
	Pt-Au	1740–1770	21.4
	Pt-Ru	1795–1780	21.0
	Pt-W	1845–1830	21.3
	Pt-Ga-In	1650–1550	19.3
	HTA (Ga+In+Cu)	1550–1650	–
	S + 2 (Ga)	1600–1640	19.5
900	Pt-Ir	1800–1780	21.5
	Pt-3Co-7Pd	–	20.4
	Pt-Pd	1755–1740	20.5
	Pt-Pd-Cu	*ca.* 1740	–
	Pt-Au	1755–1710	21.3
	Pt-Pd-Au	–	–
	Pt-W	*ca.* 1900–1860	20.3
	Pt-5Pd-5W	1860	20.9
850	Pt-Ir	1820–1800	21.5
	Pt-Pd	1750–1730	20.0
	Pt-W	*ca.* 1980–1940	19.5
800	Pt-Ir	*ca.* 1845–1800	21.5

[a]Data taken from Maerz (12), Corti (23, 24) and elsewhere

4. Jewellery Alloys: 2000 to the Present

There have been several studies to develop improved platinum jewellery alloys in the past two decades. These have focused on either stronger (harder) alloys or improved investment casting alloys, although alloys suitable for additive manufacturing ('3D printing') technology have also been of interest.

4.1 Stronger, Harder Alloys

The resistance of jewellery to abrasion and knocks (wear and scratch resistance) depends to a large extent on the hardness of the alloy. As noted earlier, a study of customer complaints showed platinum rings and wedding bands to be particularly prone to deformation of shape (misshapen) and to heavy wear (scratches and dents) during customer service (i.e. whilst being worn), when made in soft to moderately hard alloys. Hard alloys tend to be difficult to work in manufacture, especially to set gems in mounts, and so it is advantageous if an alloy is relatively soft whilst being manufactured into a piece of jewellery but can be subsequently hardened to improve its durability whilst being worn by the customer. This can be achieved by age hardening of suitable alloys after manufacture, a treatment involving the precipitation of a dense dispersion of fine particles of a second phase within the matrix grains.

For platinum, it has been noted that some current alloys are age-hardenable and alloys containing gallium have been developed specifically for this purpose. The first was the Pt-3Ga-1.5In alloy developed by Johnson Matthey (7) and others have also followed such as the HTA alloy (8) developed by Imperial Smelting and the 'S' alloys developed by Steven Kretchmer, USA (13) and discussed by Maerz (12). Weisner, in a paper presented in 1999 (38), discussed heat-treatable alloys and noted earlier work at Degussa, Germany; C. Hafner, Germany; Johnson Matthey (platinum-gallium-indium) and Steven Kretchmer (platinum-gallium-palladium) to develop heat-treatable 950 platinum alloys. He noted that all were ternary alloys, many with melting ranges much lower than the conventional binary alloys, suggesting they all contain gallium or indium additions. Such alloys are useful for their spring properties in springs and clasps, for example.

Research by Biggs *et al.* carried out at Mintek, South Africa, in 2005 examined potential platinum alloy systems with additions of 7% or less for harder jewellery alloys to identify suitable binary alloy systems that can be substantially age-hardened (39). Over 20 alloying metals were studied in the preliminary trials at levels of addition of 2% and 4%. Those showing promise were also studied at the 3% addition level. From this work, alloys with additions of titanium, zirconium, tin, gallium, germanium, magnesium, indium and vanadium were studied in more depth. From this, along with consideration of other aspects, it was concluded that the best alloy was a Pt-2Ti alloy which had as-cast and annealed hardnesses sufficiently low to be easily worked and formed, while subsequent heat treatment could increase the hardness value by about HV90. Interestingly, there are parallels here with the development of 990 gold (Au-1Ti) alloy (40, 41). The Mintek work does not appear to have been further developed into a commercial alloy, possibly because it does not show much advantage over the existing commercial gallium-containing alloys. Titanium tends to oxidise away when the alloy is remelted, so it is not easily recyclable. Also, at 98% purity, it does not fit the fineness standards of platinum jewellery, i.e. it is not pure platinum nor 950 or 900 fineness.

More recently, a harder, general-purpose alloy, TruPlat^{TM} (42), has been introduced to the market in the USA by Hoover & Strong. It is a 950 platinum-ruthenium-gallium alloy that is not age-hardenable. It has a higher work hardening rate compared to 950 platinum-ruthenium, with an annealed hardness of HV180.

4.2 Improved Casting Alloys

The motivation here is to develop alloys less prone to casting defects, particularly casting porosity. Use of alloys with lower melting temperature ranges to inhibit mould reaction is desirable too. Work carried out by Fryé at Techform, USA, and Klotz and coworkers at FEM, Germany, (33–37, 43–48) on platinum cast in shell and conventional phosphate-bonded moulds focussed on which alloys are best in terms of casting porosity formation, form-filling and surface quality and establishing the mechanical properties of cast alloys. The use of computer simulation of the casting process has also assisted in optimising process parameters in casting. Fryé has also shown the benefits of a hot isostatic pressing (HIP) treatment post-casting to remove porosity from castings and improve mechanical properties. The growing number of new platinum casting alloys that feature in these studies is particularly noticeable. This alloy development started a little earlier, in 1997.

In a paper presented at the 1997 Platinum Day symposium in New York (49), Lanam, Pozarnik and Volpe reported on a new investment casting alloy, 950 platinum-copper-cobalt, developed at Engelhard, USA, that combined the good properties of Pt-5Co and Pt-5Cu and reduced the issue of magnetism in platinum-cobalt alloy. Its as-cast hardness was about HV119, somewhat lower than Pt-5Co. Porosity was still present and it had a tendency to form a surface oxide on heating.

Another alloy development was presented by Normandeau in 2000 (50). He reported on a new 950 platinum hard casting alloy (HCA) with an as-cast hardness of HV160–170, much higher than Pt-5Co alloy. Little detail was given on the composition but the discussion in the paper pointed to it being a 950 platinum-gallium-iridium alloy, since he provided data on the gallium-to-iridium ratio and its effect on hardness.

A further alloy development was presented by Grice and Cart in 2002 (51). The development of a 950 platinum-gold-X alloy, PlatOro^{TM}, was reported as an alternative to Pt-5Co. This had an as-cast hardness of HV125, a little softer than Pt-5Co alloy, but was non-magnetic and had a lower melting temperature range of 1590–1629°C. This did not appear to be the platinum-gold-indium alloy examined by Fryé and Klotz (47) and Maerz and Laag (52) (**Table V**) since the melting temperature ranges and hardness values were different. This latter platinum-gold-indium alloy was developed at C. Hafner GmbH (53). Grice has since reported (42) that the PlatOro^{TM} alloy was actually a platinum-gold-copper alloy but is no longer commercially produced.

Fryé and Fischer-Buehner, in their study reported in 2011 (35), recognised the inadequacies of the existing commercial casting alloys and widened their search to include three newer versions that contained undisclosed elements, which they designated as hard alloys (HV175 or greater). These are included in **Table V**. The platinum-cobalt-X hard alloy with unknown additions appeared to show some promise. The platinum-ruthenium-X alloy is now known to be the platinum-ruthenium-gallium

Table V The Range of Alloys Studied in Casting Trials Since 2000

Alloy	Melting range, °C	Hardness, as cast, HV	Study (Reference)
95Pt-5Co	1655–1680	135	Fryé and Fischer-Bühner (35)
95Pt-R5u	1780–1795	130	
90Pt-10Ir	1780–1790	110	
95Pt-Pd-X[a]	1620–1685	130 soft, 220 hard	
95Pt-Ru-X	1710–1750	180	
95Pt-Co-X	1640–1670	175	
90-Pt-10Ir	1780–1800	~125	Maerz and Laag (52)
95Pt-Au-In	1640–1680	~160	
95Pt-5Co	1765–1750	~135	
95Pt-Cu-Ga	1655–1700	~168	
95Pt-5Ir	1780–1790	~83	
95Pt-5Ru	1780–1795	~150	
95Pt-5Ir	–	Soft (<120)	Fryé and Klotz (47)
90Pt-10Rh	–	Soft	
95Pt-Cu-Co	–	Soft	
95Pt-5Cu	–	Soft	
90Pt-10Ir	–	Soft	
95Pt-5Co	–	Medium–hard (120–150)	
95Pt-5Ru	–	Medium–hard	
95Pt-Au-In	–	Hard (>150)	
95Pt-Ru-Ga	–	Hard	
95Pt-Cu-Ga	–	Hard	
95Pt-Co-In	–	Hard	
95Pt-Ru-Ga-X	–	Hard	

[a]X = additional elements unknown at time of publication of referenced paper

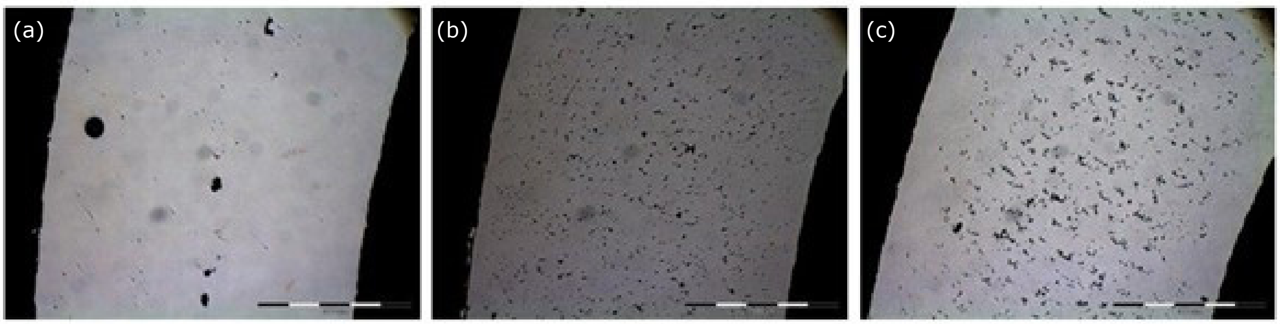

Fig. 3. Porosity in cast platinum alloys: (a) 950 platinum-cobalt; (b) 950 platinum-ruthenium; (c) 950 platinum-ruthenium-indium (35)

alloy from Hoover & Strong (51). The platinum-cobalt-X alloy is a platinum-cobalt-indium alloy from Legor (54) and is harder and non-magnetic compared to platinum-cobalt. **Figure 3** shows porosity in some of the alloys studied in this work.

In 2014, Klotz *et al.* at FEM utilised computer simulation of casting and thermodynamic calculations to optimise the process parameters of casting Pt-5Ru and Pt-5Co alloys (44). It was significant in that ternary alloys of 950 platinum-cobalt-ruthenium were explored. Improved form-filling and surface quality resulted from additions of cobalt to platinum-ruthenium alloys, the optimum amount depending on casting technique used: centrifugal or tilt casting.

Maerz and Laag (52) studied six alloys in their 2016 study (**Table V**) which used tilt casting (as opposed to centrifugal casting) in their trials.

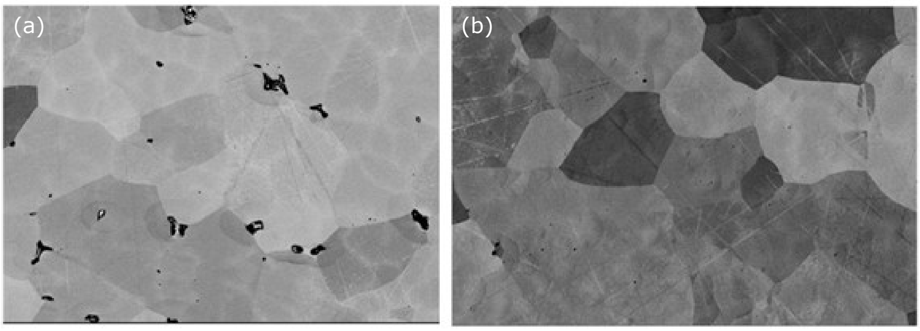

Fig. 4. Porosity in cast 950 platinum-ruthenium: (a) as-cast; (b) after HIP (47)

Table VI Alloys Documented in the Mechanical Properties Database (48)

Alloy	Hardness, as cast, HV	Hardness, as cast and HIPed, HV	Category
95Pt-5Ir	79	81	Soft (<120 HV)
90Pt-10Rh	89	89	Soft
95Pt-Cu-Co	111	110	Soft
95Pt-5Cu	112	114	Soft
90Pt-10Ir	113	117	Soft
95Pt-5Co	129±12	122	Medium–hard (120–150 HV)
95Pt-5Ru	129±8	125	Medium–hard
95Pt-1.8Au-2.7In-0.5Ru	165	163	Hard
95Pt-3.5Ru-1.5Ga	166	156	Hard
95Pt-2Cu-3Ga	166	156	Hard
95Pt-4Co-1In	167	164	Hard
95Pt-2Ru-3Ga	207	190	Hard
95.5Pt-2.5Ru-2Co	133	121	Medium–hard
95.5Pt-3.5Ru-1Co	129	128	Medium–hard
95.5Pt-3Pd-1.5Co	91	82	Soft

Two contained gallium or indium and these alloys showed higher as-cast hardness and were rated high in terms of castability. Each alloy had different strengths and weaknesses and the authors concluded that no alloy was perfect but that progress was being made. It was noted that C. Hafner patented an alloy in 2013, 950 platinum-gold-indium, with the use of iridium or ruthenium as grain refiners (53), which was probably the alloy referred to in **Table V**. This alloy has a lower melting temperature which was claimed to facilitate good casting and to have less porosity. It also had a good hardness, HV 160–170 depending on the grain refiner used.

The largest range of alloys was studied by Fryé and Klotz (**Table V**) who also measured mechanical properties and wear resistance of castings (47). They warned against use of soft alloys in cast jewellery and noted pronounced microsegregation in gallium- and indium-containing alloys which increased microshrinkage porosity. HIP treatment ('HIPing') after casting eliminated porosity and restored ductility, **Figure 4**. They also noted wear was related to hardness, with harder alloys wearing less.

It is clear from the foregoing that no new alloy completely met the desired casting requirements, although a database of mechanical properties of many of the casting alloys was established by Klotz and Fryé for alloys in the as-cast and in the HIPed condition (48). This database has data on 13 compositions at 950 fineness and two at 900 fineness. As well as the conventional compositions described in **Tables III** and **V**, it also includes some newer ternary and quaternary compositions, as shown in **Table VI**, which only lists the hardness values; perhaps it also clarifies some of the unknown compositions documented in **Table V**.

A more fundamental approach to improved casting alloy design was undertaken recently by Professor Glatzel and his coworkers at the University of Bayreuth, Germany, and Richemont International SA, Switzerland (55). They looked to develop an improved casting alloy of 950 fineness with the following requirements:

- Low casting temperature
- Small melting range
- Microstructure that is homogenous, fine-grained (100–150 μm) and with low porosity
- Hardness in range HV 155–170 for wear resistance and good ductility (>30%)
- Good reflectance with a bright surface
- Alloying elements that are biocompatible and recyclable.

Their benchmark alloy was 95Pt-1.8Cu-2.9Ga which was a recent alloy development (see **Tables V** and **VI**). Excluding allergenic, radioactive and toxic elements, 25 possible alloying elements were selected and ranked according to a suitability index which comprised four characteristics: maximum solubility in platinum (C_{max}); hardness index (H_i); melting interval index (M_{ii}) and liquidus temperature change index (T_{lci}). From these, a first iteration of five alloys were selected for testing and following this, a second set of five alloys were selected for testing. Casting was performed in a tilt casting machine. These alloys contained up to five alloying elements from a list including aluminium, gold, copper, chromium, iron, iridium, manganese, palladium, rhodium and vanadium. From these 10 alloys, two in the second iteration were found to be the most promising (**Table VII**).

It is very evident that these compositions are radically different from those listed in **Tables V** and **VI**. They have hardnesses of HV164 (A2) and HV165 (B2) respectively compared to HV225 for the benchmark platinum-copper-gallium alloy. It will be interesting to see if these or similar alloys are developed to commercial status and find a niche among the current alloys. With the base metal alloying elements including iron and manganese, it is possible there may be tarnishing issues with such alloys, if we compare the experiences in developing alternative white gold compositions with manganese and iron additions.

4.3 Alloys for Additive Manufacturing

The development of additive manufacturing of jewellery has attracted much interest in the industry in recent years and considerable research and development has been carried out on machine technology, build techniques and suitable alloys. The technology involves selective laser melting (SLM) of successive layers of alloy powders, and it has become evident that such powders need to be tailored in composition to suit the process. Alloying additions of high vapour pressure metals are not desirable, for example. In the field of carat golds, it is also important to reduce reflectivity and thermal conductivity or diffusivity to better absorb energy and inhibit heat loss through the metal, thus enhancing consolidation of the powders during laser melting. Examples of modifying carat gold alloy compositions have been discussed by Klotz *et al.* (56). Regarding platinum alloys, these tend to have considerably lower thermal conductivities as has been discussed by Wright in terms of laser welding (26) and Zito in terms of additive manufacturing of jewellery (57). Zito also noted that reflectivities are lower than gold and silver. Work at Progold SpA, Italy, on SLM of 950 fineness platinum jewellery has been reported by Zito and his coworkers (57–60). In his 2014 paper (57), Zito used an unspecified 950 platinum alloy powder while in his 2015 paper (59), Zito used a 950 platinum alloy powder "with alloying additions slightly different from the cobalt-containing alloy used in the preceding work" but gives no further details other than to say it was not doped with semiconductor elements to reduce thermal conductivity (as was done with the carat gold alloys in his work). In the 2018 paper, in which jewellery made by SLM was compared to the same pieces made by investment casting (60), Zito noted the items produced by casting and by SLM were made in the same 950 platinum-copper-gallium-indium alloy but gave no details on actual composition. This was different from

Table VII The Compositions of the Two Most Promising Alloys (55)

Alloy	Pt, wt%	Cu, wt%	Fe, wt%	Pd, wt%	Mn, wt%	Cr, wt%	V, wt%	Y, wt%
A2	95	1.3	1.2	–	1.1	1.1	–	–
B2	95	0.3	1.0	1.5	–	–	1.8	0.1

the casting alloys discussed in the earlier section, in that it contained indium as well as copper and gallium.

More recently, Klotz and König (61) have reported research on additive manufacturing by the laser powder bed fusion (LPBF) process of platinum jewellery items. LPBF is an alternative description for the SLM process. In this research, they were concerned with optimising process parameters and used the commercial 950 platinum-gold-indium alloy made by C. Hafner (52). They showed parts could be made successfully with a residual porosity of below 0.1%.

Thus, it appears that there is little need to develop special alloy compositions suited to additive manufacturing technology; the conventional alloys are acceptable and do not appear to pose any major problems.

4.4 Other Alloys

To conclude this paper, we note other recent alloy developments in the patent and other literature that do not fit into the three preceding categories. For example, European Patent applications from Heimerle + Meule GmbH, Germany (62) describe alloys that have optimised processing properties at 950 and lower finenesses based on platinum-tungsten-copper–(ruthenium/rhodium/iridium) and described as having high hardness and abrasion resistance. The ruthenium/rhodium/iridium additions act as grain refiners.

Another patent from the watchmaker, Omega SA, Switzerland (63), concerns 950 platinum alloys that are cobalt- and nickel-free, based on platinum-iridium-gold-germanium-(ruthenium/rhodium/palladium/tin/gallium/rhenium) that have mechanical properties that meet the criteria for watchmaking whilst having the colour and luminosity of platinum-iridium alloys.

As many platinum alloys are alloyed with other pgms and precious metals which are inherently expensive, there is a concern in the jewellery industry about cost. This begs the question of developing lower cost alloys as discussed by Williams in terms of platinum alloys over a range of finenesses, aimed at the US market (64). He cited examples of such alloys (such as platinum-10% copper which work hardens too rapidly) and noted that they often have properties that are not suitable for jewellery manufacture. He noted current alloys such as 950 Pt-5Co, Pt-5Cu and Pt-5W that do meet the lower cost criterion but cautioned that processing costs may increase. He concluded that lower fineness alloys are often not feasible due to technical and commercial constraints.

5. General Discussion

As has been noted earlier, the platinum alloys used for jewellery in the early 20th century were based on industrial alloy compositions, typically alloyed with other pgms. Platinum-iridium alloys were particularly popular. The real growth in popularity of platinum jewellery began in Japan in the 1960s and then worldwide in the 1970s, when platinum became more widely available and the producers set up their marketing arm, Platinum Guild International. This led to the realisation that these current alloys did not fulfil all the needs of the jewellery industry in terms of the technical properties needed for the manufacturing technologies in use and for the performance of the jewellery in service. Examples of such needs include investment (lost wax) casting, mechanical machining processes and harder alloys for better wear and scratch resistance and to retain a polished surface.

This led to the development of new alloys to meet these needs such as the platinum-5% cobalt alloy for investment casting and the use of gallium additions to produce age-hardenable alloys (as well as improved processing technologies). As discussed by Huckle (10) and Maerz (12) in their reviews, the available alloys provided a wide range of properties to suit the various manufacturing processes in use and complied with the various fineness standards of countries around the world. They also noted that different alloys for manufacturing processes were preferred in the various countries. An example was the adoption of Pt-5Co as the preferred casting alloy in Europe, while the USA preferred Pt-10Ir, although Pt-5Co was making some inroads. Japan had its own preferred alloy compositions. It is worth noting here that the jewellery industry is typically very conservative in adopting new manufacturing technologies, including alloys.

More recently, Raykhtsaum has reviewed platinum alloys in terms of their phase diagrams and properties to explore some industrial alloys that could potentially be used for jewellery manufacture (65). He found that some ternary alloy systems including platinum-palladium-ruthenium, platinum-iridium-rhodium, platinum-rhodium-ruthenium and platinum-gold-rhodium had potential in terms of good mechanical properties, corrosion resistance and colour. He also considered that Pt-5Ni and Pt-10Ni alloys could be suitable as they are non-magnetic and have good mechanical properties (Pt-10Ni is potentially age-hardenable as there is an order-disorder transformation at this composition). However, he did not take into consideration the nickel release characteristics which could inhibit its use under the European Union (EU) Nickel Directive regulations. Interestingly, the ternary alloy systems do not appear to have been developed into commercial alloys, possibly due to cost considerations.

Investment casting has developed as a major manufacturing process in the jewellery industry since the 1950s, but investment casting of platinum jewellery has been particularly challenging. Major reasons for this are the much higher melting temperature ranges of platinum alloys (compared to gold and silver) that necessitates use of phosphate-bonded refractories for moulds, coupled with the inferior flowability (viscosity) of molten platinum alloys that requires centrifugal casting technology to get good mould filling and limits casting tree size. Surface quality and porosity are also significant problems in the production of good quality castings, the former being an aspect of metal-mould reaction during casting. It is, therefore, not surprising that improved investment casting alloys have been the focus of much research over the past 20–30 years. A major aspect has been the need to reduce the melting temperature range to minimise these problems and thus the use of gallium and indium additions to reduce melting temperatures has been a strong feature in new alloy development.

A more fundamental alloy design approach to casting alloys, undertaken by Glatzel and coworkers (55), led to alloy compositions at 950 fineness that are markedly different, as reported in **Table VII**. These are possibly aimed more at watch applications rather than jewellery but may point to another direction in jewellery alloy development.

Many conventional platinum alloys tend to be soft in the annealed and as-cast conditions and this leads to premature wear and scratch damage during service as well as deformation of shape. Harder, stronger alloys result in improved wear and scratch resistance, as well as an ability to better retain a polished surface and enable thinner cross-sections in more elegant designs. Some alloy developments to produce harder alloys has been seen. The ability to manufacture a jewellery piece when in a soft condition and subsequently age-harden it to produce better service performance is attractive to jewellery manufacturers and this has led to the development of several gallium-containing alloys that are age-hardenable. Again, a more fundamental approach to harder and stronger alloys was undertaken at Mintek in South Africa and resulted in a platinum-2% titanium alloy as the most promising. This development does not appear to have been taken further commercially to an alloy that complies with the 950 fineness standard for jewellery application.

It was noted earlier in this section that the jewellery industry tends to be very conservative in adopting new technology. Swann reviewed progress in the industry in 2002 (66) to mark the 10th Platinum Day symposium, the first having been held in New York, USA, in 1995. As well as reviewing the market growth in various countries, he focused particularly on the US market. He remarked that the Platinum Day symposia had helped promote technical aspects: new equipment, processes and alloys. For example, he noted the progress in investment casting from vertical spin casting machines to modern vacuum centrifugal casters with increased melt charge size up to 500 g using induction melting; also, the progress in computer numerical control (CNC) machining and use of extruded tube. Swann also noted that in the Platinum Day symposia, only 18% of presentations had been on platinum alloys compared to 67% on process developments. He interpreted this as indicating that the range of alloys available in 2002 offered a good compromise of workability and economic use. He further noted that in the USA platinum-ruthenium was the preferred alloy for machining platinum wedding bands while platinum-iridium or platinum-cobalt was preferred for casting and platinum-iridium for hand manufacture. He noted the difference with European preferences and that in Asia platinum-palladium was preferred, but as the palladium price increased it was thrifted with copper or cobalt, echoing the reviews of Huckle and Maerz a few years earlier. He discussed the advantages of the preferred US alloys in technical and economic terms. However, he noted a switch from Pt-10Ir to Pt-4.8Ru for general purpose alloys as the industry, led by Tiffany & Co, USA, decided to focus on 950 fineness alloys. He was somewhat tepid on new alloy introductions but, as this review has demonstrated, since the time of his presentation, considerable alloy development has been undertaken. It remains to be seen how successfully they endure in commercial practice!

To conclude this discussion, it is appropriate to note some non-conventional platinum alloys that are of potential interest for jewellery application. Bulk metallic glasses (BMGs), also known as amorphous metals, are of interest for jewellery application because of their inherent high ductility and the ability to process material using polymer processing technology such as blow or vacuum moulding. Work on gold and platinum-based BMGs has been reported by Lohwongwatana and Schroers (67) in which the development of an 850 fineness platinum alloy was described. More recently, Houghton and Greer at the University of Cambridge, UK, reviewed the research in this field carried out to date (68, 69). Developing platinum BMG alloys that meet the fineness standards for jewellery is a significant problem and, technically, tarnishing appears to be an issue that inhibits its application.

6. Conclusions

There has been an evolution of, and growth in, platinum alloy compositions for jewellery application since the 1920s, with a focus on developing alloys suited to the manufacturing technologies in current use. Until the advent of the 21st century, most platinum alloys for jewellery were based on existing industrial alloys, with platinum-iridium alloys favoured during the early part of the 20th century. There have been some significant alloy developments over the past 25–30 years aimed at improving strength and hardness and improving investment casting quality. There is now a wide range of alloys available at 950 and 900 fineness standards with a spectrum of properties. Of note has been the development of heat treatable alloys containing gallium.

The investment casting of platinum alloys remains a major issue in terms of surface quality and defect formation, particularly gas and shrinkage porosity. The use of HIP post-casting removes porosity and improves mechanical properties. To date, no perfect casting alloy has been identified to replace the universally accepted Pt-5Co alloy.

There has been a major evolution in platinum alloys, particularly for investment (lost wax) casting application, in the first two decades of the 21st century. A recent substantial, structured alloy development approach has produced some significantly different casting alloys containing up to five alloying metals. It remains to be seen if these prove to be superior. The new manufacturing technology of additive manufacturing ('3D printing') does not appear to require special alloy compositions in contrast to carat golds.

Acknowledgements

This paper is adapted and developed from an earlier presentation made at the Jewellery Technology Forum, Vicenza, Italy in January 2022. I would like to thank many colleagues and companies in the industry for information and allowing use of pictures and tables. These include Teresa Fryé of Techform, USA; Ulrich Klotz of FEM, Germany; Jurgen Maerz, formerly of Platinum Guild International, USA; Stewart Grice of Hoover & Strong, USA; Joerg Fischer-Buehner of Legor, Italy; Johnson Matthey, UK; and Progold, Italy.

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