THE EVOLUTION OF PLATINUM ALLOYS FOR JEWELLERY APPLICATION OVER THE LAST CENTURY

Dr. Christopher W. Corti
COReGOLD Technology Consultancy
Reading, UK

INTRODUCTION

Platinum has only been known to Europe since the 16th century with rumours of the existence of a white metal, platina, in central and south America that cannot 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 Indians of Ecuador and Colombia in NW 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 of the separation of the PGMs was developed and its metallurgy researched and understood. The interest in using platinum as a jewellery metal developed from this time but its popularity really grew in the mid-late 20th century, and 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 last 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 %.

It is worth noting that the main interest in platinum and its alloys over the last century (and longer) has been for industrial applications: MacDonald and Hunt[1] have detailed these developments in their book on its history. Platinum is a precious and rare metal that is very ductile, tough, corrosion resistant, chemically unreactive and 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.

JEWELLERY ALLOYS: THE 1920s TO THE 1990s

The popular use of platinum in jewellery dates from the late 19th to early 20th century, often as a basis for diamond (and other precious gems) jewellery. Smith, in his book[2] published in 1933, notes its use in jewellery at 99.5% Pt purity (995 fineness) with small additions of alloying metals to harden it, including iridium (Ir), rhodium (Rh), ruthenium (Ru), gold (Au), silver (Ag) and copper (Cu). He also notes that the platinum standard (in the UK) is 950 fineness (i.e. parts per thousand) and is finding general acceptance. The term 'platinum' is deemed to include iridium. He further notes that much of the platinum in use in jewellery is 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 jewellery alloys tended to be based on the 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 manufacture of jewellery, particularly investment (lost wax) casting, difficult and challenging for the jeweller used to gold and silver. Raykhtsaum[3] has recently reviewed selected literature on platinum alloy systems used in industry and for jewellery, Table 1, with a focus on their metallurgy and properties. A range of mechanical properties is possible, but he notes that the legal requirements on minimum platinum content for jewellery limits the alloy range and prohibits the utilization of enhanced mechanical properties of many alloys outside this range.

Table 1: Platinum alloy systems reviewed by Raykhtsaum[3]

Alloy System	Comments	Ternary additions
Pt-Pd	Soft alloys	Ru increases hardness
Pt-Ir	Harder/stronger than Pt-Pd. Commonly used in jewellery at 5% & 10% Ir	Rh enhances mechanical properties
Pt-Rh	Soft, ductile alloys	Ru enhances strength but loss of ductility
Pt-Ru	Harder/stronger. Commonly used in jewellery	
Pt-Au	Miscibility gap & spinodal decomposition a feature. Au is a very effective hardener, but ductility drops due to grain growth during solution treatment	Rh enhances hardness/ strength & 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	

A further issue to the use of platinum alloys in jewellery has been the lack of accurate analysis techniques. This meant that its acceptance as a hallmarkable jewellery metal[4] in the UK came much later in 1975.

From this time, with its now much wider availability, platinum was promoted by the platinum producers as a rare, high value jewellery metal and 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 this marketing, coupled with growth in usage, led to some alloy development such as the 950-fineness platinum- 5% cobalt alloy for investment casting[5] and the use of gallium additions to produce heat treatable alloys[6] with higher strength and hardness, as Normandeau has reported.[7] For example, one European platinum producer listed only 4 alloys for jewellery application in their internal alloy catalogue dating to the late 1980s, all at 950 fineness, namely platinum – copper, platinum – cobalt, platinum -ruthenium and platinum-gallium-indium. The copper alloy is listed as a general-purpose alloy (i.e. suitable for wrought fabrication and casting applications) and the cobalt alloy is listed as suitable for investment casting. Another European producer lists only 3 alloys at 950 fineness: Pt-5Cu, Pt-5Co/Ni and Pt-5Ru.

The work to develop the 950-fineness platinum – cobalt alloy for casting has been described by Ainsley, Bourne and Knapton[5] in 1978; they actually developed it as a platinum–4.5% cobalt alloy, and 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 mold refractories and reduces the likelihood of metal-mold 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 reported on the development of platinum alloys to overcome production problems at the 1996 Santa Fe Symposium.[8] 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 notes that, in Japan, Pt-Pd alloys are in common use, particularly Pt-10%Pd, whereas in Europe Pt-5% Cu is preferred but that it is not a good casting alloy whereas for casting application Pt-5%Co is finding success. In the USA, he notes Pt-10%Ir is commonly in use as an all-purpose alloy (i.e. suitable for wrought fabrication and casting) and that Pt-5%Ru is used where a hard, good machining alloy is needed. He also notes Pt-5% Co is finding growing use for casting applications in the USA.

Maerz (Platinum Guild International) also reviewed platinum jewellery alloys at the 1999 Santa Fe Symposium,[9] and this built on the information provided by Huckle. It sums 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, United Kingdom 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, Netherlands and Spain). In Germany, he noted that several fineness standards ranging from 800, 900 and 950, 960 to 999.

In the USA, he noted that the standard for jewellery to be marked as platinum was 950 fineness but that the minimum amount of platinum allowed was 500 parts per thousand with the rest of the alloy platinum group metals (PGMs), in total comprising 950 parts per thousand with a zero tolerance. He also notes that 950,900 and 850 fineness standards are allowed in Japan.

Table 2: Platinum jewellery alloys around the world in 1999 (from Maerz[9])

Fineness standard	Alloy	Hardness, HV	Application	Country
950	Pt-Ir	80	All-purpose, Casting. Soft alloy	D, J, USA
	Pt-Co	135	Casting (slightly magnetic)	D, Eu, HK, J, USA
	Pt-Co-Cu	120	Casting, malleable (non-magnetic)	USA
	Pt-Cu	120	General-purpose (96Pt-4Cu)	D, Eu, HK
	Pt-Pd	60	Soft alloy – fine detailed casting	J, HK, Eu
	Pt-Pd-Ru		Chainmaking (4Pd-1Ru)	J
	Pt-Au	90 Aged 300	All-purpose, soft but heat treatable	General use worldwide
	Pt-Ru	130	Tubing for wedding bands	Eu, HK, USA
	Pt-W	135	Spring alloy. Heat-treatable	D, Eu
	Pt-Ga-In	225	3Ga-1.5In Heat-treatable. Hard alloy. Machining tube, springs	General use worldwide
	'HTA'	175-185 Aged340-360	4.8 (Ga+In+Cu). Heat-treatable	General use worldwide
	S + 1 S + 2	135-145 Aged 252 170 - 200 Aged 306	Contain Ga. Heat-treatable	General use worldwide
900	Pt-Ir	110	All-purpose; Work horse in USA	USA, J, D
	Pt-Co-Pd	150	Hard casting alloy 3Co-7Pd	J only
	Pt-Pd	80	All-purpose. Greyish colour; needs Rh plating. Chainmaking	J, HK
	Pt-Pd-Cu	110	3-5% copper improves hardness and workability	Asia
	Pt-Au	135	All-purpose	Eu, J, S. Africa
	Pt-Pd-Au		Similar but softer than 900 Pt-Au	
	Pt-W	350	Hard alloy, findings, etc	UK
	Pt-Pd-W	150	All-purpose	Asia
850	Pt-Ir	160	Findings, etc	J
	Pt-Pd	90	Soft, chainmaking	J, HK
	Pt-W	251	Spring alloy, heat-treatable	UK
	Pt-Pd-Co	150	Harder Pt-pd alloy for Asia	J
	Pt-Pd-Cu		Chainmaking (8Pd-7Cu or 10Pd-5Cu)	J
800	Pt-Ir	200	Hard alloy, mesh & chain	D only

Eu – Europe, D – Germany, HK – Hong Kong, J – Japan, UK – United Kingdom

Co – cobalt, Cu – copper, Au – gold, Ir – iridium, Pd – palladium, Ru – ruthenium, W -tungsten, Ga – gallium, In – indium

All-purpose/general-purpose— suitable for wrought fabrication and casting, Aged – precipitation hardened by heat treatment

Regarding actual alloy compositions, he notes that each alloy is made for specific manufacturing functions. Some alloys are preferred for tubing or machining and others for casting, for example, and there are differences in preference in different countries. Table 2 lists the alloys in common (or growing) usage around the world with their function and countries of major use. He also lists separately several alloys that are specific to Japan, and these are included in the Table.

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 does note that, in the USA, the most common alloys in use are 950 platinum with 5% cobalt or ruthenium and 900 platinum with 10% iridium. However, in an updated later version of this paper,[10] the Pt-5Cu alloy is included in the general alloy list.

These reviews do not include the alloys in use in the old USSR. In his book published in 1984, Savitskii[11] notes only two 950 fineness alloys are in use – Pt-5 Ir in Russia and Pt-4.5 Pd – 0.5 Ir in East Germany (GDR).

TECHNICAL ASPECTS OF ALLOYS: The 1920s to the 1990s

From the list of alloys summarised in Table 2, 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 may benefit from rhodium plating, e.g. Pt-10% Pd alloy, to give a brighter, whiter colour. The main differences lie in their hardness/strength and melting ranges.

Battaini has examined the microstructure of several platinum alloys[12] and notes 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 Pt-Au and Pt-Cu 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, Fig 1(a), where an aged hardness of HV300 can be attained, leading to better scratch and wear resistance, but its use in as-cast 950Pt-Au rings has not been observed,[13,14] suggesting it is a treatment not in common use. Platinum-cobalt, Fig 1(b), forms an ordered intermetallic compound, Pt3Co, 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 Pt-Ga phase diagram, Fig 2, as well as lowering melting temperature ranges and its use forms the basis of several heat treatable alloys as noted earlier and listed in Table 2. Indium also has a similar effect in lowering the melting temperature range and is being used in several newer alloys, as will be described later.

The development of age-hardenable alloys using gallium additions stems from the late 1970s. The work of Bourne and Knapton[6] led to the development of the 950 platinum – 3% gallium – 1.5% indium alloy. In their patent, they also refer to Pt-Ga-Au alloys as an option, with the use of yttrium additions of about 0.1% as a deoxidizer. The alloy Pt-3Ga-2Au is claimed to have a high hardness of HV200. Such gold-bearing alloys are said to cast well. Interestingly, whilst such Pt-Ga-Au alloys of the invention are said to be suitable for springs, there is no mention in the patent of heat treatments to age harden the Ga-containing alloys.

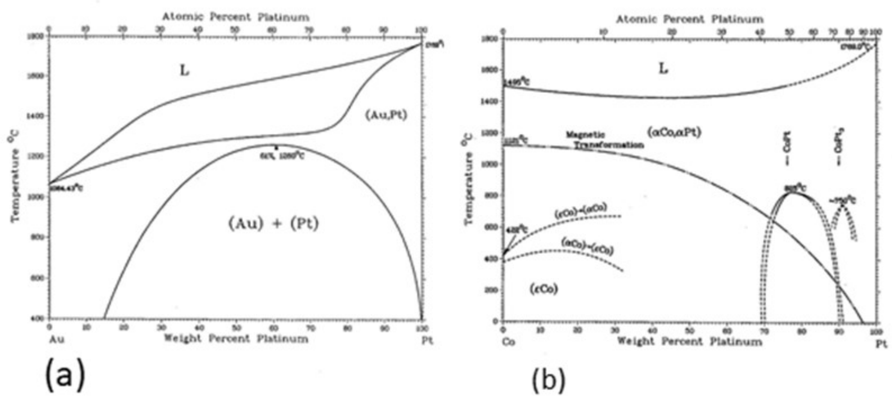

Figure 1: Phase diagrams (a) platinum–gold and (b) platinum–cobalt

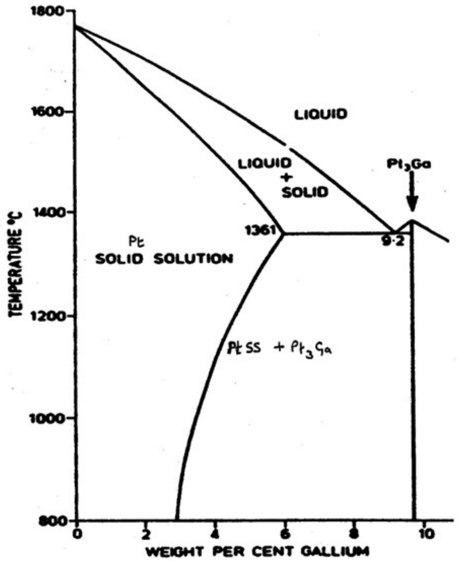

Figure 2: Platinum–gallium partial phase diagram

This early work has subsequently led to the development of other Ga-containing alloys that are claimed to be heat treatable. Normandeau & Ueno (Imperial Smelting) reported that Pt alloys with tungsten, gold, gallium, indium, or copper are age-hardenable by heat treatment and they described their research to develop their HTA alloy which is a 950 platinum–4.8% (Ga-In-Cu) alloy which can be age-hardened to HV340-360 and up to HV420-430 if aged in the cold-worked condition.[7] Kretchmer has also developed gallium-containing alloys[15] including 950Pt-Ga-Pd that can be age-hardened to HV320. A further patent describes the age-hardening treatment of Pt-Ga-Pd alloys[15] that involves solution treatment at 982°C (1799°F) or higher and followed by an ageing treatment at 593°-649°C (1099°-1200°F). This work stems from research[16] reported in 1998.

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 usually when in the age-hardened condition. In a recent study by the author of customer complaints,[13,14] it has been 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.

Table 3: Physical properties of platinum alloys

Fineness standard	Alloy	Liquidus – Solidus temperatures, °C	Density, g/cm³
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	ca1740-	-
	Pt-Au	1755-1710	21.3
	Pt-Pd-Au	-	-
	Pt-W	ca1900-1860	20.3
	Pt-5Pd-5W	1860 -	20.9
850	Pt-Ir	1820-1800	21.5
	Pt-Pd	1750-1730	20.0
	Pt-W	ca1980-1940	19.5
800	Pt-Ir	ca1845-1800	21.5

Data taken from Maerz[9] and Corti[18,20] and elsewhere.

Work around the turn of the 21st century and summarised in recent reviews[17,18] has 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 micro-alloys do not appear to have been 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 (3216°F), considerably higher than gold (1064°C/1947°F) and silver (961°C/1761°F). Its alloys tend to have similarly high melting temperature ranges, as shown in Table 3, 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- 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,[19] as platinum tends to gall (adhere) on the tool. The low thermal diffusivity of platinum alloys makes welding easier, particularly laser welding[21] 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[22] and the poor melt fluidity requires use of centrifugal casting machines[23] 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[8,23-24,28] and there have been several investigations on the relative merits of different alloys,[5,25-28] 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[28] at Stuller Settings Inc in 1998, comparing its casting behavior 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-5%Co alloy to be the best of current alloys but still not ideal.

JEWELLERY ALLOYS: 2000 TO THE PRESENT

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

Stronger, harder alloys

The resistance of jewellery to abrasion and knocks – wear and scratch resistance – depends largely 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 – 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-3% Ga-1.5% In alloy developed by Johnson Matthey[6] and others have also followed such as the HTA alloy[7] developed by Imperial Smelting and the ‘S’ alloys developed by Kretchmer[16] and discussed by Maerz.[9] Weisner, in a paper[29] presented in 1999, discusses heat treatable alloys and notes earlier work at Degussa, C Hafner, Johnson Matthey (Pt-Ga-In) and Kretchmer (Pt-Ga-Pd) to develop heat-treatable 950-platinum alloys. He notes that all are ternary alloys, many with melting ranges much lower than the conventional binary alloys, suggesting they all contain gallium and/or indium additions. Such alloys are useful for their spring properties in springs and clasps, for example.

Research by Biggs et al[30] carried out at Mintek, South Africa in 2005 has examined potential platinum alloy systems for harder jewellery alloys to identify suitable binary alloy systems that can be substantially age-hardened. Over 20 alloying metals were studied in the preliminary trials at levels with addition of 2% and 4% and those showing promise were also studied at the 3% addition level. From this work, alloys with additions of titanium (Ti), zirconium (Zr), Tin (Sn), gallium (Ga), germanium (Ge), magnesium (Mg), indium (In) and vanadium (V) were studied in more depth. From this, along with consideration of other aspects, it was concluded that the best alloy was a Pt-2% Ti alloy which had as cast and annealed hardnesses sufficiently low to be easily worked and formed but, with subsequent heat treatment, the hardness value could be increased by about HV90. Interestingly, there are parallels here with the development of 990Gold (Au-1%Ti) alloy.[31] 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 for platinum jewellery, i.e. it is not pure platinum nor 950 or 900 fineness.

More recently, a harder, general-purpose alloy, TruPlat™, has been introduced to the market in the USA by Hoover & Strong. It is a 950 Pt-Ru-Ga alloy that is not age-hardenable. It has a higher work hardening rate compared to 950 Pt-Ru, with an annealed hardness of HV180.

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 and Klotz and co-workers at FEM on platinum cast in shell and conventional phosphate-bonded moulds has 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.[26-27,32-35] 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 in removing porosity from castings and improving mechanical properties. What is particularly noticeable is the growing number of new platinum casting alloys that feature in these studies. This alloy development started a little earlier in 1997.

In a paper presented at the 1997 Platinum Day symposium in New York, Lanam, Pozarnik and Volpe[36] reported on a new investment casting alloy, 950 Pt-Cu-Co, developed at Engelhard, that combines the good properties of Pt-5Co and Pt-5Cu and reduces the issue of magnetism in Pt-Co alloys. It's as-cast hardness is about HV119, somewhat lower than Pt-5Co. Porosity was still present, and it tended to form a surface oxide on heating.

Another alloy development was presented by Normandeau in 2000 in which he reported[37] on a new 950 platinum Hard Casting Alloy (HCA) with an as-cast hardness of HV 160-170, much higher than Pt-5Co alloy. Little detail is given on the composition but the discussion in the paper points to it being a 950Pt-Ir-Ga alloy, since he provides data on the Ga:Ir ratio and its effect on hardness.

A further alloy development was presented by Grice & Cart[38] in 2002 where the development of a 950 Pt-Au-X alloy, PlatOro™, is reported as an alternative to Pt-5Co. This has an as-cast hardness of HV125, a little softer than Pt-5Co alloy but is non-magnetic and has a lower melting temperature range of 1590°-1629°C (2894°-2964°F). This does not appear to be the Pt-Au-In alloy examined by Fryé & Klotz[34] and Maerz and Laag,[39] Table 4, since the melting temperature range and hardness values are different. This latter Pt-Au-In alloy was developed at C Hafner GmbH.[40] Grice has since reported[41] that the PlatOro™ alloy is actually a Pt-Au-Cu alloy but is no longer commercially produced.

Table 4: 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 & Fischer-B (27)
95Pt-R5u	1780-1795	130	
90Pt-10Ir	1780-1790	110	
95Pt-Pd-X	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 & Laag (39)
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 & Klotz (34)
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	

X - additional elements unknown

Fryé and Fischer-Buehner, in their study[27] reported in 2011, recognised the inadequacies of the existing commercial casting alloys and widened their search to include 3 newer versions that contained undisclosed elements, which they designated as hard alloys (HV175 or greater). These are included in the table of alloys reported in Table 4. The platinum-cobalt- X hard alloy with unknown additions appeared to show some promise. The Pt-Ru-X alloy is now known to be the Pt-Ru-Ga alloy from Hoover & Strong,[38] and the Pt-Co-X alloy is a Pt-Co-In alloy from Legor[42] and is harder and non-magnetic compared to Pt-Co. Figure 3 shows porosity in some of the alloys studied in this work.

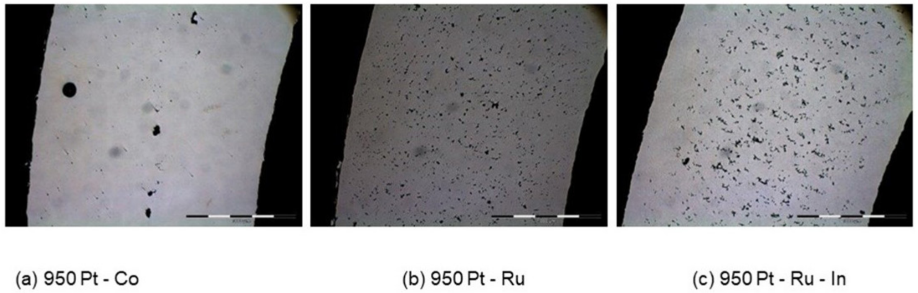

Figure 3: Porosity in cast platinum alloys, L-R: (a) 950 Pt-Co, (b) 950 Pt-Ru, (c) 950 Pt-Ru-In (from Fryé & Fischer-Buehner[27])

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[33] and was significant in that ternary alloys of 950 platinum-cobalt-ruthenium were explored. Improved form-filling and surface quality resulted from additions of Co to Pt-Ru alloys, the optimum amount depending on casting technique used— centrifugal or tilt casting.

Maerz and Laag[39] studied six alloys in their 2016 study, Table 4, which used tilt casting (as opposed to centrifugal casting) in their trials. 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 is noted that C Hafner patented an alloy, 950 Pt-Au-In in 2013, with the use of Ir or Ru as grain refiners,[40] which is probably the alloy referred to in Table 4. This alloy has a lower melting temperature which, it is claimed, facilitates good casting and has less porosity. It also has a good hardness, HV 160 -170 depending on the grain refiner used.

The largest range of alloys was studied by Fryé and Klotz, Table 4, who also measured mechanical properties and wear resistance of castings.[34] They warned against the use of soft alloys in cast jewellery and noted pronounced micro-segregation in Ga- and In-containing alloys which increased micro shrinkage porosity. Hot isostatic pressing treatment (HIPing) after casting eliminated porosity and restored ductility, Figure 4. They also noted wear was related to hardness, 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.[35] This database has data on 13 compositions at 950 fineness and two at 900 fineness. As well as the conventional compositions described in Tables 3 and 4, it also includes some newer ternary/quaternary compositions, as shown in Table 5, where only the hardness values are listed; perhaps, it also clarifies some of the unknown compositions documented in Table 4.

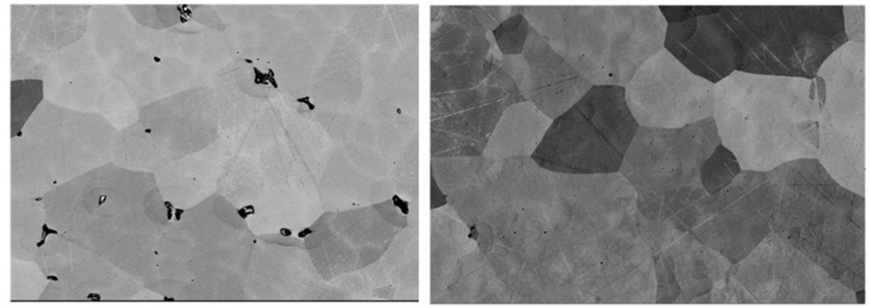

Figure 4: Porosity in cast 950 Pt-Ru, L-R: (a) as-cast, (b) after hot isostatic pressing (HIP) (from Fryé & Klotz[34])

Table 5: Alloys documented in the Mechanical Properties Database, (Klotz & Fryé[35])

Alloy	Hardness- As cast, HV	Hardness – As cast and HIPed, HV	Category
95Pt-5Ir	79	81	Soft (<120)
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)
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

A more fundamental approach to improved casting alloy design[43] has been undertaken recently by Professor Glatzel and his co-workers at the University of Bayreuth and Richemont

International. 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 the 95Pt-1.8Cu-2.9Ga which is a recent alloy development (see Tables 4 & 5). 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 Al, Au, Cu, Cr, Fe, Ir, Mn, Pd, Rh and V. From these 10 alloys, two in the second iteration were found to be the most promising, Table 6. It is very evident that these compositions are radically different from those listed in Tables 4 and 5.

They have a hardness of HV 164 (A2) & 165 (B2) respectively compared to HV 225 for the benchmark Pt-Cu-Ga alloy. It will be interesting to see if these or similar alloys are developed to commercial status and find a niche amongst 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.

Table 6: The compositions of the two most promising alloys (from Glatzel et al[43])

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

Pt- platinum, Cu -copper, Fe – iron, Pd – palladium, Mn – manganese, Cr – chromium, V – vanadium, Y -yttrium. Compositions in wt.%.

Alloys for Additive Manufacturing (3D Printing)

The development of Additive Manufacturing (3D printing) of jewellery has attracted much interest in the industry in recent years and considerable R & D has been carried out on developing 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 karat golds, it is also important to reduce reflectivity and thermal conductivity/diffusivity to better absorb energy and inhibit heat loss through the metal, thus enhancing consolidation of the powders during laser melting. Examples of modifying karat gold alloy compositions have been discussed by Klotz et al.[44] Regarding platinum alloys, these tend to have considerably lower thermal conductivities, as has been discussed by Wright in terms of laser welding[21] and Zito in terms of 3D printing of jewellery.[45] Zito also notes reflectivity is lower than gold and silver. Work at Progold on laser selective melting of 950 fineness platinum jewellery has been reported by Zito and his co-workers.[45-48] In his 2014 paper,[45] Zito used an unspecified 950 Pt alloy powder whilst in his 2015 paper,[47] 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 karat gold alloys in his work). In the 2018 paper, in which jewellery made by SLM is compared to the same pieces made by investment casting,[48] Zito notes the items produced by casting and by SLM were made in the same 950 Pt-Cu-Ga-In alloy but gives no details on actual composition. This is different from the casting alloys discussed in the earlier section, in that it contains indium as well as copper and gallium.

More recently, Klotz and König[49] have reported research on additive manufacturing by the laser powder bed fusion (LPBF) process of platinum jewellery items. In this research, they were concerned with optimising process parameters and used the commercial 950Pt- Au-In alloy made by C Hafner.[40] 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 3D printing technology; the conventional alloys are acceptable and do not appear to pose any major problems.

Other Alloys

To conclude this paper, it is noted there are other recent alloy developments that appear in the patent and other literature that do not fit into the 3 preceding categories. For example, European Patent applications from Heimerle and Meule[50] describe alloys that have optimised processing properties at 950 and lower fineness based on Pt-W-Cu –(Ru/Rh/Ir) and described as having high hardness and abrasion resistance. The Ru/Rh/Ir additions act as grain refiners.

Another patent[51] from the watchmaker Omega SA concerns 950 platinum alloys that are cobalt- and nickel-free, based on Pt-Ir-Au-Ge- (Ru/Rh/ Pd/Sn/Ga/Re) that have mechanical properties that meet the criteria for watchmaking whilst having the colour and luminosity of Pt-Ir 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 and this has been discussed by Williams in terms of platinum alloys over a range of fineness, aimed at the USA market.[52] He cites examples of such alloys (such as Pt-10% Cu which works hardens too rapidly) and notes that they often have properties that are not suitable for jewellery manufacture. He notes there are current alloys such as 950 Pt-5Co, Pt-5Cu and Pt-5W that do meet the lower cost criterion but cautions that processing costs may increase. He concludes that lower fineness alloys are often not feasible due to technical and commercial constraints.

To complete this section, I will report on very recent research on developing improved platinum alloys for jewellery application. This has been undertaken by a company in the UK, Alloyed Ltd, which has expertise in designing alloys from the fundamental properties of metals using complex computer modelling technology. The original basis for the work was to develop an improved alloy for investment casting. This has led to a patent[53] which describes the alloy composition in terms of complex equations, and it is difficult to determine what the preferred compositions are from the claims. Since the initial work, Anglo Platinum has taken an interest and guided the development in terms of optimising the composition (which is now nickel- and cobalt-free) and marketing it as an improved alloy with good workability and castability. It is notably harder and has a lower melting range and improved melt fluidity. The alloy, Innoveo Platinum, was launched commercially[54] in May 2024; it is a 950-platinum alloy containing ruthenium plus other alloying metals. Its lower melting temperature would suggest it contains low melting point metals, possibly Ga and/or In. We await a full technical report on its development, properties and application. It would appear to be an improved casting alloy with lower levels of porosity claimed.

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 and mechanical machining processes and harder alloys for better wear and scratch resistance and to retain a polished surface.
This led to the initial 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 being developed). As discussed by Huckle[8] and Maerz[9] 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 such manufacturing processes were preferred in the various countries. An example here is the adoption of Pt-5Co as the preferred casting alloy in Europe whilst the USA industry preferred to remain with 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[55] 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. He found that some ternary alloy systems including Pt-Pd-Ru, Pt-Ir-Rh, Pt-Rh-Ru and Pt-Au-Rh had potential in terms of their good mechanical properties, corrosion resistance and colour. He also considered 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 does not take into consideration the nickel release characteristics which could inhibit its use under the 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 last 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 co-workers,[43] has led to alloy compositions at 950 fineness that are markedly different, as reported in Table 6. These are possibly aimed more at watch application rather than jewellery but may point to another direction in jewellery alloy development. Further work using this alloy design approach by Alloyed Ltd and Anglo Platinum has led to the recent development of Innoveo Platinum which appears to be a general-purpose alloy but with good casting properties.

Many conventional platinum alloys tend to be soft in the annealed and as-cast condition and this leads to premature wear and scratch damage during service as well as deformation of shape. Harder, stronger alloys result in improved wear & 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 also 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/stronger alloys was undertaken at Mintek in South Africa and has resulted in a Pt-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 is noted earlier in this section that the jewellery industry tends to be very conservative in adopting new technology and it is interesting to note that, in 2002, Swann reviewed progress in the industry,[56] to mark the 10th Platinum Day symposium, the first being held in New York in 1995. As well as reviewing the market growth in various countries, he focuses particularly on the USA market. He remarks that the Platinum Day symposia have helped in promoting the technical aspects – new equipment, processes and alloys. For example, he notes the progress in investment casting from vertical spin casting machines to modern vacuum centrifugal casters with increased melt charge size up to 500g using induction melting; also, the progress in CNC machining and use of extruded tube. Swann also notes that in the Platinum Day symposia, only 18% of presentations have been on platinum alloys compared to 67% on process developments. He interprets this as indicating that the range of alloys currently available in 2002 offer a good compromise of workability and economic use. He further notes that in the USA Pt-Ru is the preferred alloy for machining platinum wedding bands whilst Pt-Ir or Pt-Co is preferred for casting and Pt-Ir for hand manufacture. He notes the difference with European preferences and that in Asia Pt-Pd was preferred but as Pd price increased this was thrifted with copper and/or cobalt, echoing the reviews of Huckle and Maerz a few years earlier. Regarding alloy preferences in the USA, he discusses the advantages of these alloys in technical and economic terms. However, he notes a switch from Pt-10Ir to Pt-4.8Ru for general purpose alloys as the industry, led by Tiffany & Co., decided on focus on 950 fineness alloys. He is 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[57] in which the development of an 850-fineness platinum alloy was described. More recently, work at Cambridge University by Houghton and Greer has reviewed the research in this field carried out to date.[58,59] 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. Research on platinum-based BMGs has been presented by Klotz and co-workers at FEM in 2023.[60]

CONCLUSIONS

1. 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 the existing industrial alloys with the platinum -iridium alloys favoured in the early part of the 20th century.
2. There have been some significant alloy developments over the last 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.
3. 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 hot isostatic pressing post casting removes porosity and improves mechanical properties. To date, there is no improved casting alloy identified to replace the universally accepted Pt-5Co alloy.
4. There has been a major evolution in platinum alloys, particularly for investment (lost wax) casting application, in the last two decades (21st century). Recent developments, using a structured alloy design approach, has produced some significantly different casting alloys containing up to 5 alloying metals. It remains to be seen if these prove to be superior.
5. The new manufacturing technology of additive manufacturing (3D printing) does not appear to require special alloy compositions in contrast to the karat golds.

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REFERENCES

1. D McDonald & L B Hunt, "*A History of Platinum and its allied metals*", 1982, Johnson Matthey, Chapter 1. ISBN 0 905118 83 9
2. E A Smith, "*Working in Precious Metals*", 1933. Reprinted 1978, N.A.G. Press Ltd. Chapter 15. ISBN 7198 0032 3
3. G Raykhtsaum, "Platinum alloys: A selective review of the literature", *Platinum Metals Review*, 2013, vol 57 (3), 202-213
4. J S Forbes, "*Hallmark – A history of the London Assay Office*", 1998, Unicorn Press/The Goldsmiths' Company, Chapter 12. ISBN 0 906290 26 0
5. G Ainsley, A A Bourne & R W E Rushforth, "Platinum Investment Casting Alloys", *Platinum Metals Review*, 1978, vol 22(3), 78-87
6. A A Bourne and A Knapton, US patent US4165983A, 1979/ UK patent GB58258A, 1981
7. G Normandeau & D Euno, "Understanding Heat Treatable Platinum Alloys", 1999, Proc. *Santa Fe Symposium*, ed

D Schneller, Met-Chem Research Inc, 73-103. See also ibid,1998, Platinum Day symposium, New York, Platinum Guild International, vol 5, 35-41, 1998

8. J Huckle, "The Development of Platinum Alloys to overcome Production Problems", 1996, Proc *Santa Fe Symposium*, ed D Schneller, Met-Chem Research Inc, 301-325. See also: J Huckle, "Choosing platinum alloys to maximise production efficiency", Platinum Day symposium, 1995, Platinum Guild International, vol 1, 2-6,
9. J Maerz, "Platinum Alloy Applications for Jewelry", 1999, Proc. *Santa Fe Symposium*, ed D Schneller, Met-Chem Research Inc, 55-71,
10. J. Maerz, "Platinum Alloys – Features and Benefits",2004, Platinum Guild International. Download from the Ganoksin website: www.ganoksin.com/article/platinumalloys-features-benefits)
11. E M Savitskii, "*Handbook of Precious Metals*", English edition ed. A Prince, 1989, Hemisphere Publishing Corp., Chapter 6. ISBN0 89116 709 9. Originally published in Russian in 1984.
12. P Battaini, "Metallography of Platinum and Platinum Alloys", 2010, Proc. Santa Fe Symposium, ed E Bell, Met-Chem Research Inc, 27-49. Also: ibid, *Platinum Metals Review*, 2011, vol 55(2),74-83
13. C W Corti, "Jewellery – Is it fit for Purpose? An Analysis based on examination of customer complaints", Presented at the Jewellery Technology Forum, Held at Vicenza, Italy, January 2018 (download from Legor/JTF website)
14. C W Corti, "Jewelry – Is it fit for purpose? An analysis based on customer complaints", 2018, Proc. *Santa Fe Symposium*, Ed E Bell, Met-Chem Research Inc, p163-175
15. S Kretchmer, US Patent 6562158, May 2003 "Heat treatable platinum-gallium-palladium alloys for jewelry" and US Patent 5846352, December 1998, "Heat treatment of a platinum-gallium alloy for jewelry".
16. S Kretchmer, "Plat/S+™. Innovative general purpose platinum alloy transforming goldsmiths into platinum smiths", Platinum Day Symposium, Newport Beach, Platinum Guild International, vol 4, 35-38,1998,
17. C W Corti, "Microalloying of High Carat Gold, Platinum and Silver", presented at the Jewellery Technology Forum, Vicenza, Italy, 17-18th June 2005. Publ. in conference proceedings.

18. C W Corti, "Jewellery Alloys – Past, Present and Future", Keynote lecture presented at the 1st Jewellery Materials Congress, Goldsmiths Hall, London, July 2019.
19. R W E Rushforth, "Machining Properties of Platinum", *Platinum Metals Review*, 1978, vol 22 (1), p2-12
20. C W Corti, "Basic Metallurgy of the Precious Metals – Part 1", 2017, Proc *Santa Fe Symposium*, Ed E Bell, Met-Chem Research Inc, 25-61 and 2023, Proc *The Jewelry Symposium*, Minneapolis, ed J Bell Cast, 2025, p 67-110
21. J C Wright, "Laser-welding platinum jewellery", 2001, Proc *Santa Fe Symposium*, ed E Bell, Met-Chem Research Inc, p455-468. See also J C Wright, "Jewellery-related properties of platinum", *Platinum Metals Review*, 2002, vol 46(2) 66-72
22. P J Horton, "Investment Powder Technology – The Present and the Future", 2001, Proc *Santa Fe Symposium*, Ed. E Bell, Met-Chem Research Inc, 213-239
23. J Maerz, "Platinum Casting Tree Design", 2007, Proc *Santa Fe Symposium*, Ed E Bell, Met-Chem Research Inc, 305-322
24. R Atkin, "Trouble Shooting Platinum Casting Defects and Difficulties", 1996, Proc *Santa Fe Symposium*, Ed D Schneller, Met-Chem Research Inc, 327-337.
25. P Lester, S Taylor & R Süss, "The Effect of different investment powders and flask temperatures on the casting of platinum alloys", 2002, Proc *Santa Fe Symposium*, Ed E Bell, Met-Chem Research Inc, 321-334.
26. U Klotz & T Drago, "The role of process parameters in Platinum Casting", 2010, Proc *Santa Fe Symposium*, ed E Bell, Met-Chem research Inc, 287-325 and references therein. Also, ibid, *Platinum Metals Review*, 2011, vol 55(1), 20-27
27. T Fryé & J Fischer-Buehner, "Platinum alloys in the 21st Century: A Comparative Study", 2011, Proc *Santa Fe Symposium*, Ed E Bell, Met-Chem Research Inc, 210-229 and references therein. Also ibid, "The Quest for quality: Optimising platinum casting for 21st century needs", *Platinum Metals Review*, 2012, vol 56(3),155-161. An updated version also presented at the Jewellery Materials Congress, London, July 2019
28. G Todd, D Busby, D Launey, M Linscomb, G Gilman, "A Review of cast platinum jewelry fabrication methods", Platinum Day Symposium, Newport Beach, Platinum Day

Symposium, Platinum Guild International, vol 4, 39-47, 1998

29. K Weisner, "Heat treatable platinum for jewelry", 1999, Platinum Day symposium, Platinum Guild International, vol 6, 25-30
30. T Biggs, S Taylor & E van de Lingen, "The hardening of platinum alloys for potential jewellery application", Platinum Metals Review, 2005, vol 49(1), 2-15.
31. C W Corti, "Metallurgy of Microalloyed 24 carat Golds", 1999, Proc *Santa Fe Symposium*, Ed E Bell, Met-Chem Research Inc, p379-402; also ibid, Gold Bulletin, 1999, vol 32(2), 39-47
32. T Fryé, J T Strauss, J Fischer-Buehner, U Klotz, "The effects of Hot Isostatic Pressing of platinum alloy castings on mechanical properties and microstructure", 2014, Proc. *Santa Fe Symposium*, Ed E Bell & J Haldeman, Met-Chem Research Inc, 189-209
33. U Klotz, T Heiss, D Tilberto & F Held, "Platinum investment casting: Materials properties, casting simulation and optimum process parameters", presented at *Santa Fe Symposium*, 2014 but published in Proc *Santa Fe Symposium*, 2015, ed E Bell et al, Met-Chem Research Inc, p143-180. Also, ibid, *Johnson Matthey Technology Review*, 2015, vol 59(2), 95-108 & 129-138
34. T Fryé & U Klotz, "Mechanical properties and wear resistance of platinum jewelry casting alloys: A comparative study", 2018, Proc *Santa Fe Symposiu*m, ed E Bell et al, Met-Chem Research Inc, 235-273.
35. U Klotz & T Fryé, "Mechanical properties of platinum jewellery casting alloys", 2019, *Johnson Matthey Technology Review*, vol 63(2), 89-99
36. R Lanam, F Pozarnik, T Volpe, "Platinum alloy characteristics: A comparison of existing platinum casting alloys with Pt-Cu-Co", 1997, Platinum Day symposium, Platinum Guild International, vol 3, 2-12
37. G Normandeau & D Ueno, "Platinum alloy design for the investment casting process", 2000, Platinum Day symposium, Platinum Guild International, vol 8, 41-49
38. S Grice & C Cart, "PlatOro™: The perfect marriage", 2002, Platinum Day Symposium, Platinum Guild International, vol 10, 4-7
39. J Maerz & T Laag, "Platinum Alloys, Features and benefits: comparing six platinum alloys", 2016, Proc *Santa Fe Symposium*, ed E Bell et al, Met-Chem Research Inc, 335-353
40. T Laag & H-G Schenzel, C Hafner GmbH, German patent application DE10212007299A1, 17.10.2013,
41. S Grice, Private communication, June 2021
42. R Bertoncello & J Fischer-Bühner, Legor patent application ITM120110750A1, 2011 "Platinum-cobalt alloys with improved hardness".
43. T Trosch, F Lalire, S Pommier, R Völkl, U Glatzel, "Optimisation of a jewellery platinum alloy for precision casting: Evaluation of mechanical, microstructural and optical properties", 2018, *Johnson Matthey Technology Review*, vol 62(4),364-382.
44. U Klotz, D Tilberto & F Held, "Additive manufacturing of 18 karat yellow gold alloys", 2016, Proc *Santa Fe Symposium*, ed. E Bell et al, Met-Chem Research Inc, 255-272
45. D Zito, A Carlotto, P Sbornicchia et al, "Optimisation of SLM technology main parameters in the production of gold and platinum jewellery", 2014, Proc *Santa Fe Symposium*, ed E Bell & J Haldeman, Met-Chem Research Inc, 439-469
46. D Zito, V Allodi, P Sbornicchia & S Rappo, "Why should we direct 3D print jewelry? A comparison between two thoughts: Today and tomorrow", 2017, Proc *Santa Fe Symposium*, ed E Bell et al, Met-Chem Research Inc, 515-556
47. D Zito, A Carlotto, A Loggi, P Sbornicchia, D Bruttomesso & S Rappo, "Definition and solidity of gold and platinum jewelry produced using selective laser melting (SLM™) technology", 2015, Proc *Santa Fe Symposium*, ed E Bell et al, Met-Chem Research Inc, 455-491
48. D Zito, "Potential and innovation of the selective laser melting technique in platinum jewelry", 2018, Proc *Santa Fe Symposium*, ed E Bell et al, Met-Chem Research Inc, 625-684
49. U Klotz & F König, "Additive manufacturing of platinum alloys – practical aspects during LPBF of jewellery items", 2022, paper presented at the Jewellery Technology forum, 20th March 2022, Vicenza, Italy (paper available on the JTF website www.jtf.it
50. G Steiner, "Platinum Alloy for Jewelry", European patents

EP 2260116B1, 2014 and EP 209994181, 2007, Heimerle & Meule GmbH,

51. E Leoni et al, "Platinum alloy" European Patent EP3502286 (A1), 2019, Omega SA
52. B J Williams, "Are lower cost platinum alloys feasible?". 2001, Platinum Day Symposium, New York, Platinum Guild International, vol 9, 42-45
53. T Andre, J W Clark, G C Frater, (1) UK patent application GB 2599462 A, Alloyed Ltd, 6th April 2022 and (2) European patent EP4225957A1, Anglo Platinum Marketing Ltd, 16th August 2016, "A platinum alloy composition".
54. Various press articles published by National Jeweler and Jewellery Outlook.com in May 2024, and the Financial Times, Special report: Watches and Jewellery, July 2024
55. G Raykhtsaum, "Platinum Alloys", 2012, Proc *Santa Fe Symposium*, ed E Bell, Met-Chem Research Inc, 489-503
56. N Swann, "10 Platinum Days – What has changed?", Platinum Day Symposium, New York, 2002, Platinum Guild international, vol 10, 22-27
57. B Lohwongwatana, J Schroers, W L Johnson, "Liquidmetal – Hard 18k and .850 Pt alloys that can be processed like plastics or blown like glass", 2007, Proc *Santa Fe Symposium*, ed E Bell, Met-Chem Research Inc, 289-303
58. O S Houghton & A L Greer, "A conflict of fineness and stability: Platinum- and palladium-based bulk metallic glasses for jewellery: Part 1 Introduction and properties", 2021, *Johnson Matthey Technology Review*, vol 65(4), 506-518
59. O S Houghton & A L Greer, "A conflict of fineness and stability: Platinum- and palladium-based bulk metallic glasses for jewellery: Part 2 Processing, Tarnish resistance and future developments", 2021, *Johnson Matthey Technology Review*, vol 65(4), 519-534
60. U Klotz et al, "Platinum-based bulk metallic glasses for jewelry application", presented at the Jewellery Technology Forum, Vicenza, Italy, January 2023 and at *The Jewelry Symposium*, Minneapolis, USA, May 2023. In Proc *The Jewelry Symposium*, ed J Bell Cast, 2025, 207-224

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