JEWELLERY ALLOYS – PAST, PRESENT and FUTURE

Dr Christopher W Corti

COReGOLD Technology, Reading Berks., UK

INTRODUCTION

It is a privilege to be asked to present a Keynote at this inaugural Jewellery Materials Congress. Bearing in mind my metallurgy expertise and precious metals experience over the last 40 years, I thought it appropriate to talk about precious metal jewellery alloys. In considering what to talk about, several questions that sprang to mind included the following: Do we fully understand their metallurgy? Are they optimised to suit modern manufacturing processes? Do they meet the demands of the customer in terms of performance in service as well as decorative effect? What are the current deficiencies? Has there been much change over the years? Will there be much change in the future years? These are questions which I will attempt to answer in this presentation.

As I have lectured on jewellery alloys and modern manufacturing technologies to jewellers around the world, it has been apparent that there is a strong perception in our traditionally conservative industry that nothing much has changed over the years in terms of precious metal alloys for jewellery application. A little reflection suggests that is not true. How else can the major jewellery technology conference in the USA – the Santa Fe Symposium - sustain itself successfully for over 33 years, if there have been no changes in alloys and processes? What is the point of substantial research and development if there are no improvements? I noted in a recent consultancy with an international jewellery company in Asia that we covered over 20 topics relating to alloy developments and processes and that was principally focussed on gold alloys. The truth of the matter is that there has been change – significant change - and change continues to happen.

I am going to start this presentation by looking at the ancient past, then follow this up by the recent past. This will naturally lead into the present day situation and will highlight the advances that have been made and some deficiencies that I consider still need to be addressed. This should allow me to conclude the presentation with a look into the future! I will note here that some technology advances, interesting as they are, have not led to commercial success and I will make reference to these where appropriate.

Those of you familiar with my work in the jewellery sector will know that gold tends to be a dominant interest among all the precious metals, but I will try and cover all jewellery precious metal alloys in a balanced way. In talking about alloys, I must place them into context with regard to changes in manufacturing processes and innovative jewellery design, as well as legislative constraints. This latter includes precious metal content and alloying limitations due to factors such as health and safety. Lead and cadmium spring to mind here.

THE ANCIENT PAST

When we talk about the Ages of Man, The first – the Stone Age – is followed by the Bronze Age, a time when ancient man first started to develop and exploit metals, some 6,000 plus years ago. This was a time when man learned to alloy copper with tin to make a useful alloy we call bronze, which was sufficiently hard to make tools and weapons (and even some

jewellery). However, preceding this discovery in modern day Turkey, man discovered two metals that occurred in native form, namely gold and copper. Savitskii[1] notes that gold objects were known to the Egyptians some 12,000 years BC.

Interestingly, these two metals occur in the same period of elements [IB], along with silver and are the only two coloured pure metals. Both were too soft to be usefully used as tools or weapons but gold, in particular, was highly valued for its colour and indestructability – it did not corrode. Along with its scarcity and excellent malleability, gold became highly valued and a monetary asset, characteristics that continue to the present day. It was a metal for the ruling classes. We should also note that gold is found all over the world and has been exploited by all the ancient civilisations

In its native state, gold occurs as an impure metal, with silver as the main impurity and small amounts of copper and other metals. Typically it contains up to a few percent of silver, but other more silver-rich forms exist which are known as electrum. This contains up to 45% silver typically and is a pale yellow colour. It was known historically as white gold or green gold, as silver imparts a greenish hue and large amounts produce white gold alloys. Many ancient artefacts in gold are made from naturally -occurring electrum. The Wild Ass of Ur is made by lost wax casting in electrum and dates from 1260 BC[2] . Incidentally, lost wax casting as a manufacturing technology is some 6,000 years old. Slightly later and, perhaps the most well known of all gold artefacts is the death mask of Tutankhamun which dates from circa 1320 BC and weighs around 27kg. Analysis of this mask[3] shows it to be made of two alloy compositions, a lighter coloured 18.4 carat gold (about 76.7% gold) for the face and neck and a 22.5 carat gold (93.5% gold) for the rest of the mask.

It would have been relatively easy for ancient man to further alloy this impure gold with some copper to add strength and hardness as their melting points are similar, but the ability to make more precise alloys requires the ability to refine impure gold. This became possible relatively later in around 500 BC when the ancient Egyptians mastered the art[4].

Turning now to silver, this also dates back to the same period as gold. According to Painter in reference[5], deposits in Anatolia (Turkey) were exploited in the third millennium BC and silver supplied to Sumerian craftsmen of Asia Minor. Forbes (in reference 5) notes that silver was rarely found in the native metallic state. Rather, it was extracted from lead-silver ores such as galena by a cupellation process in which the lead and other base metals are removed by oxidation; the liquid oxides run off or pass into bone ash, leaving almost pure silver. He also notes copper has always been the preferable metal used to harden pure silver and that use continues to the present day.

In contrast, platinum and palladium appear to be more recent in history. McDonald and Hunt[6] indicate platinum was only known in Europe from the 16th century and was often described as white gold. Around this time, rumours reached Europe about the existence of a white metal, platina, in the New World - notably in central and south America - that cannot be melted . This appears to be impure platinum which is found as native metal in grains from alluvial deposits, often in association with native gold.. Such grains are mainly platinum alloyed with the other 5 platinum group metals (palladium, rhodium, ruthenium, osmium and iridium). These were exploited by pre-Colombian Indians of Ecuador and Colombia in NW South America. A number of platinum trinkets have been found in this region. A tiny ingot of platinum was analysed as about 85% platinum -4.6% palladium/rhodium/iridium - 7% iron – 1% copper. Such discoveries of trinkets and jewellery suggest that small flattened grains of platinum were consolidated by an early form of powder metallurgy using gold to liquid phase sinter the material together and form it by alternatively forging and heating it to a

homogeneous mixture. There is also evidence of gold and platinum being worked together. Two nose rings from Colombia were found to be made in native platinum-iron alloy and platinum -copper alloy containing small inclusions of osmiridium (an alloy of osmium and iridium)

It was only Wollaston's development of refining techniques in the early 1800s that enabled pure platinum (and its sister metals) to be obtained.

THE MORE RECENT PAST

To set this section into context, it is necessary to understand the legislative constraints that developed in the UK over the last 700+ years. This has been well described by Forbes[7]. This legislation was focussed initially on coinage but developed to encompass jewellery and silverwares. The aim was to develop standards for gold and silver of minimum precious metal content to prevent fraud and deception (debasement).

Table 1 Standards for Gold and Silver in the UK since 1300 (from Forbes[7])

Year	Silver	Gold	Comment
1238			Henry III Ordinance
1300	925	800 / 19.2 ct	Edward I
1478		750/ 18ct	
1500s		833/ 20 ct	Replaced 18ct standard
1526	925 & 885	916/ 22 ct	For coins only
1560	933		Sterling standard redefined
1572		18ct	Standard reverted back to 18ct
1575		22ct	In force up to 1798
1697	958.4		Britannia silver in force up to 1720
1720	925 & 958.4		Both Sterling & Britannia silver allowed
1797			Call for 14 ct gold standard to be added but not granted
1798		18ct added	Both 18 & 22 ct standards allowed
1854		9,12, 15 ct	Additional standards introduced with 18 & 22 ct
1855			All wedding rings required to be hallmarked
1932		14ct added, 12 & 15 ct dropped	4 standards : 22, 18, 14, 9ct
1942			Wedding rings, lockets, watchcases restricted to only 9ct during WWII
1999	800 & 999 standard added	990 & 999 standard added	

For silver, the use of copper to harden it dates from ancient times, as noted in the previous section. The sterling standard is believed to date from Saxon times but in 1238, an Ordinance of King Henry III directed that 'no gold shall be used of which the mark is not worth at least 100 shillings nor any silver worse than the King's money'. This was further developed by King Edward 1 in 1300 when the rudiments of the hallmarking system began. The standard

for silver was sterling, i.e. 925 fineness (92.5% silver) and that for gold was the 'Touch of Paris', i.e. 19.2 carats or 800 fineness. In 1327, the first Charter to set up the Goldsmiths Guild, now the Worshipful Company of Goldsmiths, was enacted. At various times since then these standards have been changed. Table 1 lists the standards for gold and silver up to the present day, taken from Forbes[7].

Thus, we find that silver has largely remained at Sterling 925 fineness standard with a period at a higher 933 fineness, and one in which Britannia 958 standard was the preferred standard. Currently, there are 4 standards for silver. In contrast, gold has seen varied standards, some of which have been discontinued (12 & 15 carats). Currently, there are 6 standards in operation.

In 1912, a major hoard of gold jewellery and pieces was found near to Goldsmiths Hall at Cheapside in the City of London during building excavations, A wooden box containing over 400 pieces of Elizabethan and Jacobean jewellery dating from the late 16th/early 17th century was unearthed from the premises of a goldsmith. The Cheapside Hoard, as it is known, contains rings, brooches, chains as well as other items including scent bottles and a salt cellar (and is kept at the Museum of London). Many were set with coloured gemstones and enamelled. We can presume that these stock in trade items were a mixture of new stock for sale, items being refurbished or recycled and scrap. Analysis of many of these items has been carried out by the London Assay Office and gives us a good insight into the composition of the gold alloys used in these times[8]. Over 260 XRF analyses were made.

According to the standards prevailing at this time, we would expect alloys to conform to the 18 and 22 carat standards (750 & 916 fineness) with, perhaps, some at the earlier 20 carat standard (833 fineness). The results from this investigation[8] are given in Figure 1 (3 measurements are excluded from this figure: (i) a silver- copper alloy, possibly gilt, (ii) an alloy containing 63% gold with silver and copper used for a swivel loop and (iii) an alloy containing only 39% gold with high copper and silver alloying metals.
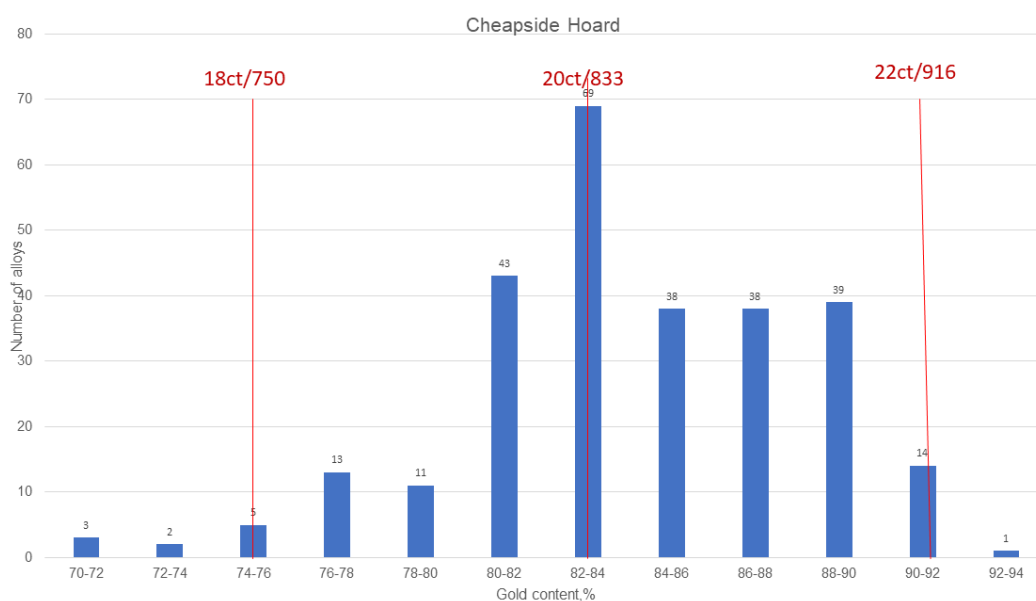

Figure 1 Histogram of measured gold contents, Cheapside Hoard

As can be seen, most of the measurements cluster around the 20 ct standard gold content (833 fineness) and higher, with relatively few at 22 ct and even less at 18ct. There is quite a wide spread of contents, suggesting that alloying technology and/or refining and assaying techniques of the time were not very accurate or consistent. The touchstone and fire assay were the main assaying techniques of the time; The touchstone is not particularly accurate[9] and it appears fire assay was also not good at that time[7]. There would be a tendency to overcarat alloys to ensure they met the standard and we should not neglect the possibility that items were surface enriched in gold by acid treatment to give a more deep colour. This could skew the XRF results upwards compared to the bulk alloy composition. All these were alloys of gold-silver-copper with small amounts of iron, typically 0.2% or less although some had higher contents, and many also with similar levels of nickel. These are probably impurities rather than deliberate alloying additions. The proportion of silver to copper also varies enormously in these alloys, typically the ratio silver:copper varying from about 4:1 to 1:4. This will have some effect on colour but probably not a large one at such high gold contents (copper tends to redden gold whereas silver bleaches the colour towards white). It will also have some effect on hardness and strength (copper is much more effective at hardening gold than silver, due to its smaller atom size.[10,11]. In terms of their metallurgy, these alloys are mostly single phase, as the majority are of high gold content, well above the 2 phase region in the ternary gold-silver-copper phase diagram[10,11,12].

THE PRESENT ERA

The understanding of the metallurgy of alloys and the effects of individual alloying metals on microstructure and properties, coupled with substantial improvements in refining technologies and assaying/analytical techniques, largely developed during the early-mid 20th century, a period when metallurgy emerged as a distinct science and technology and techniques such as X-ray diffraction and optical and electron microscopy were also developed. This is when we see the evolution of alloys with tailored properties to suit manufacturing processes and improved performance. Our knowledge at this time can be summed up in the publication of the books 'Working in Precious Metals' in 1933[13], 'Edelmetall-Taschenbuch' (the precious metals handbook) in 1967[14] and 'Gold Usage' in 1978[15]. Smith's book[13] was published at a time when such knowledge was only beginning to emerge. Smith gives many compositions of alloys that are familiar today, but, for carat golds, he notes use of additions of zinc and cadmium to Au-Ag-Cu alloys but there is no mention of grain refiners. Apart from the major precious metal companies who developed a range of commercial jewellery alloys at this time, a lot of understanding of their metallurgy was also published by research organisations such as FEM in Germany. Many phase diagrams of precious metal alloy systems were researched and published in this time, for example in references 12,14,16. This is a time when investment (lost wax) casting was re-discovered and developed and the use of grain refiners and deoxidisers became the norm.

Silver: Apart from standard Sterling 92.5% silver -copper alloy, special grades for enamelling, chain manufacture, casting and spinning were developed. These contained additions of metals such as cadmium and zinc to improve ductility, and trace additions of silicon and boron for casting alloys. Zinc also improves melt fluidity and acts as a deoxidiser in casting. For enamelling, it is necessary to limit selenium and tellurium impurity content; such impurities also cause embrittlement[17,18].

As Grimwade notes[10], the non-equilibrium solidification behaviour of sterling silver has been described by Reti[19]. A two phase structure of primary dendrites of silver-rich α-phase

surrounded by a finely-dispersed eutectic mixture of α-phase and β-phase (copper-rich) forms. This alloy is relatively soft but ductile, with a hardness of about 63HV in the as-cast state and similar in the worked and annealed condition. This rises to about 140 -180HV in the cold-worked condition. In theory, sterling silver can be age-hardened. Solution annealing at 700-730°C followed by ageing for 1hr at 300°C will increase hardness to 120-140HV. In practice, however, it is not often possible to harden sterling silver by such a precipitation hardening treatments as subsequent soldering operations causes overaging/softening and any pre-existing solder joints will melt during solution treatment[10].

One of the major drawbacks of sterling silver is the frequent occurrence of firestain. This is an internal oxidation of the copper to form sub-surface copper oxides, which show as a dark stain on the surface and is difficult to polish away. It forms on heating the metal in air, such as in annealing or soldering. As a consequence, a number of alloys that are resistant to firestain have been produced in recent times. Probably the best known of these is an alloy known as Argentium™ which contains germanium as an alloying addition[20] as well as copper. It is also more tarnish resistant, another drawback of conventional silver alloys. These alloys typically contain about 1.1% germanium and this forms an intermetallic phase, Cu_5Ge, in the microstructure and is believed to enable the formation of a protective transparent germanium oxide layer on the metal surface and inhibit internal oxidation of the copper to form firestain and retard tarnishing. Argentium™ can also be age hardened

Many of the other new commercial alloys use germanium and/or silicon additions or platinum group metal (PGM) or gold additions to confer firestain and/or tarnish resistance. Fisher-Buehner will speak about some of these developments in his presentation at this Congress[21]. Aluminium additions to silver-copper alloys have also been reported to confer firestain resistance[20] but such alloys have never found commercial interest. A review of the patent literature[22] from 1926 looked at tarnish resistance and improved strength of sterling silvers. Two periods of strong patent activity – 1926-1940 and 1989 – 2012 were noted. In the latter period, the use of PGMs (either palladium or platinum) as alloying metals were found in 5 out of 19 patents. In one, palladium is claimed to improve tarnish resistance and, in others, platinum is claimed to improve both tarnish resistance and strength.

As noted above, sterling silver is a soft and malleable alloy. There is a demand for stronger/harder alloys and a recent development by a USA company has tried to address this concern[23,24]. The alloy is a 92.5% Ag-Cu-Pd-Sn-Zn composition with 2.75% Pd. The new alloy is much harder than conventional sterling silver with an as-cast hardness of 90-110HV (compared to 65HV) and can be age-hardened to 140-170HV. It also has a superior tarnish resistance.

I will note here that 925 sterling silver dominates the UK and other markets but in others, lower fineness silvers, typically 800/830/850 are preferred.

Gold: Gold jewellery can exhibit a range of colours and hence a range of compositions exist to cover this colour range at all the standard caratages used around the world. To understand why this is, we need to understand the market and the impact of culture.

In the East, gold jewellery is still bought primarily as an investment and consequently consumers tend to buy high caratage jewellery. We find 24 ct ('Chuk Kam' – 99.0% gold minimum) in the oriental countries, 22 ct in India and the sub-continent and 21 ct in Arabic countries of the Gulf region. However, in the West, gold is bought mainly for adornment, with little regard for its value. Thus, we find that in the 'latin' language and Mediterranean 'bowl' of countries, 18 ct is the predominant choice whilst further north in the Germanic culture countries of Europe, lower caratages dominate – 14 and 8 ct in Germany, 9 ct in the

UK and 10 and 14 ct in the USA. These trends are mirrored in the Commonwealth countries and in Scandinavia, silver tends to dominate over gold! Portugal has a unique preference for 19.2 ct (80.0 % gold) jewellery.

Gold is unique among the precious metals in that its alloys can be made in a range of colours, depending on the alloying metals used. As well as its intrinsic rich yellow colour, alloying it with copper moves the colour towards pink/rose and red whilst alloying with any other white/grey metal tends to bleach the yellow colour towards white. Alloying with silver (and cadmium) gives a greenish hue to the yellow; such alloys are often referred to as green gold. At 9 and 10 ct, gold, alloying just with silver yields a good white colour but soft alloys.. This range of colours is well illustrated by the colour triangle, Figure 2, of the gold-copper-silver alloy system

Some metals, such as nickel and palladium, are strong bleachers of the colour of gold whilst others are moderate to weak bleachers of colour. Consequently, there are two commercial types of white gold – those where nickel is the main bleaching agent and those where palladium is the main whitener. Nickel produces hard alloys because of the large field of immiscibility in the Au-Ni phase diagram whereas palladium produces soft malleable alloys. The whitening effect of alloying metals in gold was quantified by O'Connor[25] and others. Since 2000, the use of nickel is restricted in the EU countries as a consequence of the EU Nickel Directive, as many people suffer from a skin allergy due to a nickel sensitivity. This limits the amount of nickel that leaches out from any metal object that is in "close and constant contact with the skin" and is defined in an artificial sweat test[26]. This tends to limit the nickel content in white gold jewellery sold in the EU countries. Many commercial alloys at 14 & 18 ct contain both nickel and palladium.

Another issue has been the colour definition of white gold as opposed to pale yellow. As many commercial white golds are not a good white colour for both technical and economic reasons, the jewellery is often rhodium plated to confer a bright white colour but there has been no definition of when a pale yellow colour becomes a white alloy.. This has been resolved through a White Gold Task Force set up by MJSA and World Gold Council[27,28] in which a white gold is defined quantitatively in terms of a parameter, the Yellowness Index, as having a YI value of 35 or less.

Returning to the various compositions of gold alloys, one European manufacturer in the latter half of the 20th century had compositions covering over 10 caratages. At 9ct, there were over 30 compositions, excluding solders, to cover a range of colours, applications and markets(manufacturing). At 18 ct, there were over 25 compositions listed

Our understanding of the coloured carat golds and the influence of composition on microstructure and properties is, perhaps, illustrated by two examples. Firstly, when 18 and lower carat golds that contain copper are annealed after cold working, simply allowing them to air-cool results in material that is hard and not as ductile as we might anticipate for recrystallised material and will tend to crack on further working. However, if the alloys are rapidly cooled by water-quenching, the alloys are soft and ductile and can be further cold worked. This is because quenching retains the high-temperature solid solution. Slow cooling below about 400°C allows the precipitation of copper-rich phases and/or the disorder to order transformation to intermetallic phases AuCu and $AuCu_3$ which are face centred tetragonal in structure. The problem does not occur in high carat 21 and 22 ct golds which remain single phase solid solutions down to room temperature.
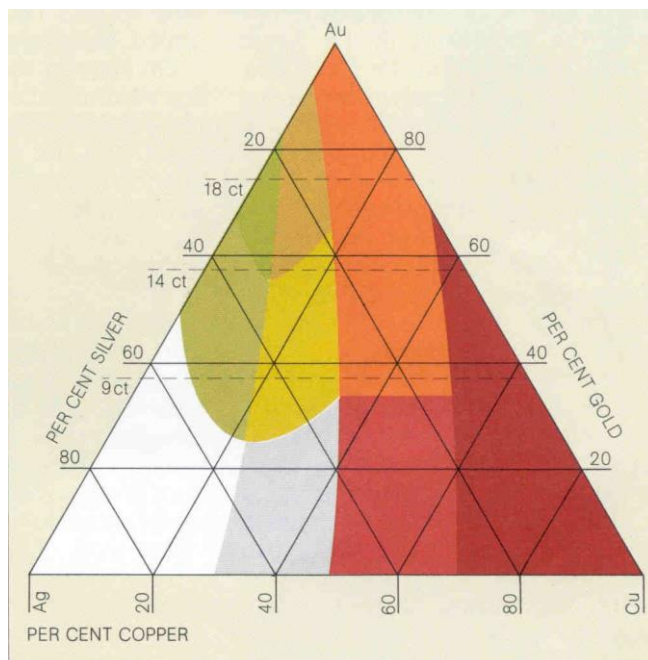
Figure 2 The Colour Triangle, schematic illustrating the range of colours in the gold-silver-copper alloy system.
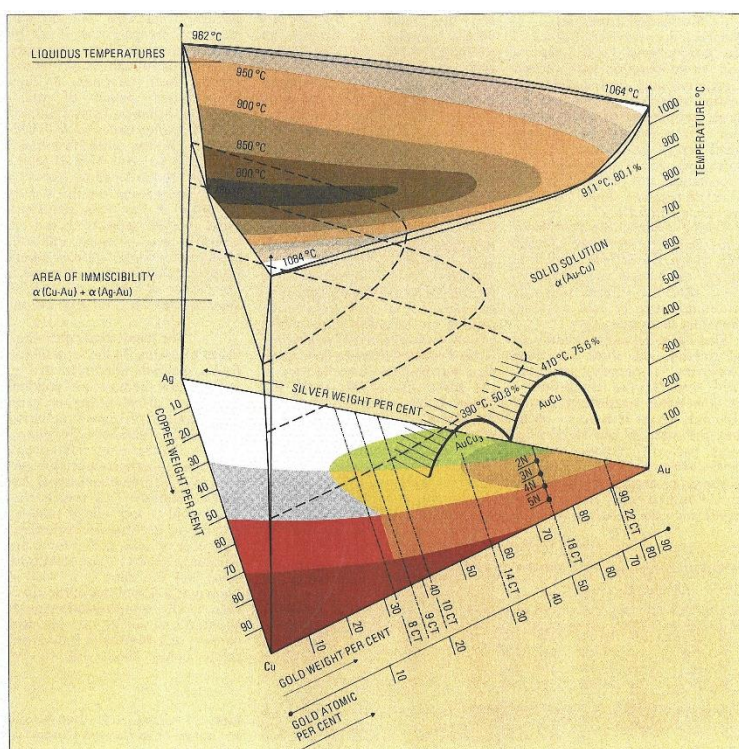

Figure 3 The Gold-Copper-Silver ternary phase diagram. Lines relating to various caratages of gold alloys are marked on the base, along with the colour variation

The second example is how changes in composition by additions of zinc to gold-copper-silver alloys influences workability/malleability. If we take the ternary phase diagram, Figure 3, it is represented by a prism with the 3 binary phase diagrams evident on each prism face.

If we take vertical slices through our prism at, say, 10, 14 and 18 carat, we have what we call pseudo binary phase diagrams, Figure 4. Again, we can see the significant region of 2 phase structures at these 3 caratages.

The amount of second phase will influence how hard and difficult to work an alloy is. The amount formed will depend on how close the composition is to the boundary with the single phase region. Close to it, there will be a little amount. In the centre, there will be lots – a 50-50 mixture. McDonald and Sistare[29] came up with a system of describing such alloys. Type I alloys are essentially single phase and are easy to work. Type II contain some second phase and are less easy to work and Type III have lots of second phase and are difficult to work. 14 carat golds can be particularly difficult to work, so careful selection of alloy composition allows us to obtain golds that are easy to work. But we then restrict ourselves in the colour range that we can get!
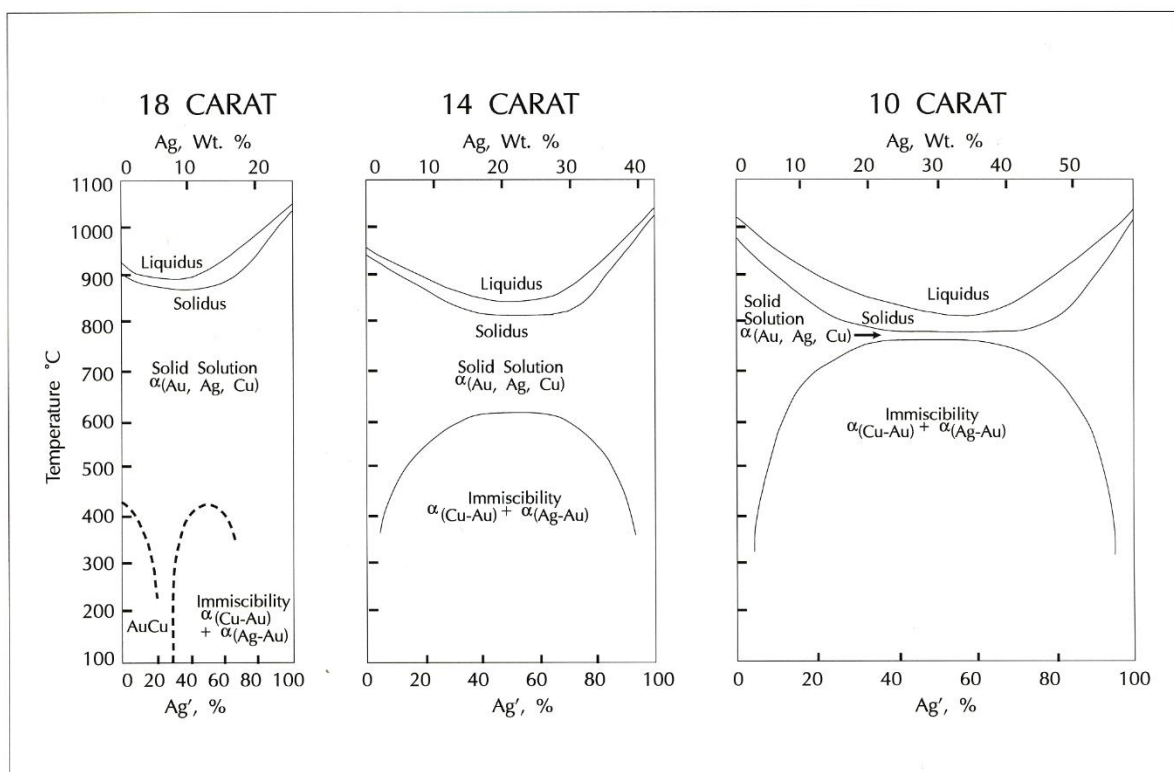

Figure 4 Pseudo binary phase diagrams for 10,14 and 18 ct golds plotted versus silver content derived from the ternary Au-Ag-Cu phase diagram (from reference 29)

However, zinc alloying additions tend to contract the region of second phase in carat golds so, if we add some zinc to our alloy, for example, we can free up the alloy in terms of workability, as Table 2 shows. All three 14 carat gold compositions are the same yellow colour, but the zinc additions change the alloy from Type III to Type II and even to Type I.

There are other aspects of carat golds such as heat treatment, susceptibility to embrittlement, cracking and hot shortness, stress corrosion cracking, tarnishing and casting defects that are

too detailed to consider here but further details can be found in the literature, e.g. references 10, 11, 18, 30. The use of grain refiners such as iridium, ruthenium and cobalt is now common, as is the use of silicon and zinc to confer fluidity and mould-filling in investment casting.

Table 2 Effect of composition of 14 ct yellow golds on workability

Gold, wt%	Silver, wt%	Copper, wt%	Zinc, wt%	Type*
58.5	26.5	15.0	-	III
58.5	8.3	29.1	4.1	II
58.5	4.0	31.2	6.3	I

* After MacDonald & Sistare (29)

Platinum: Whilst the popular use of platinum in jewellery dates from the early 20th century, the lack of accurate analysis techniques meant that its acceptance as a hallmarkable jewellery metal was delayed until 1975**.** Thus early alloys tended to be based on the industrial alloys and comparatively little development of specific jewellery alloys has been carried out.

Compared to the carat golds, platinum jewellery alloys are generally of high fineness, typically 900 and 950 (although there are lower finenesses such as 585 being promoted) and, with alloying contents of only 5 or 10%, are metallurgically more straightforward, as Battaini has demonstrated[31]. Most are single phase solid solution alloys, although some are two phase and can be age hardened. Table 3 shows some properties of common alloys used worldwide. They are typically simple binary or ternary alloys. As can be seen, melting range varies widely. Some alloys such as the 5% palladium alloy are quite soft whilst others are quite hard. The 5% cobalt alloy is considered to be the best commercial casting alloy, which is, perhaps, related to its narrow melting range. Its high hardness reflects the fact that it is a 2 phase alloy with some $CoPt_3$ as the hardening phase. It is also slightly magnetic. Colour does not vary much with alloy composition. The age-hardenable alloys contain gallium, which has a limited solid solubility in platinum of about 6% maximum but which drops to around 2.5% at lower temperatures. This enables precipitation hardening by the Pt_3Ga phase on heat treatment, as Normandeau has discussed[32].

Much platinum jewellery is produced by investment (lost wax) casting and is prone to casting porosity[33] which is undesirable. The use of hot isostatic pressing (HIPing) of castings has been shown to be effective in removing porosity[34] and improving microstructure. In another study of customer complaints, cast platinum jewellery was often made in soft alloys that led to deformation, heavy wear and breakages[35]. The mechanical properties of conventional alloys in the cast condition have recently been reported[36] and highlights a wide spread of properties and the benefits of HIPing on microstructure, strength and ductility.

There is a clear view in the industry that the current platinum casting alloys are not optimum for this process and some progress has been made in improved alloy compositions[37]. More recently, in a more structured approach to alloy design, some improved alloys have been developed[38]. In this research, potential alloying elements were ranked in terms of a 'Suitability Index' which is derived from 4 characteristics: maximum solubility in platinum, hardness index, melting interval index and liquidus temperature change index. From this, 5 alloy compositions were identified as promising, compared to a reference platinum – copper-

gallium alloy. From this work, two promising compositions were identified based on Pt-Cu-Fe-Mn-Cr and Pt-Cu-Fe-Pd-V-Y. Both have an as-cast hardness of about 165HV. It will be interesting to see if these alloys gain commercial acceptance.

Table 3 Properties of some common platinum jewellery alloys

Alloy	Density g/cm^3	Melting range, °C	Hardness, HV	Applications
5% iridium	21.4	1780 – 1790	80 ann 140 c.w.	High work hardening; Catches & springs General purpose
10% iridium	21.5	1780 – 1800	110 ann	
5% palladium	20.6	1755 - 1765	60 ann	Castings, delicate settings
10% palladium	19.8	1740 - 1755	80 ann	General purpose
5% palladium + 5% copper	<20	~1740	110 ann	General purpose
5% gold	21.3	~ 1730-1750	90 ann 300 aged 400°C	General purpose Hardenable
5% ruthenium	20.7	1780 – 1795	120-130 220- 230 c.w.	General purpose
5% cobalt	20.8	1750 – 1765	135 270 c.w.	Casting
5% copper	20.0	1725 – 1745	120 108 cast	General purpose
4.8% gallium + indium + copper 'HTA'	-	1550 – 1650	280 cast 175-185 ann 340 – 360 c.w. 340 – 360 aged 700°C	Springs Heat treatable
1.5% indium + 3.0% gallium	19.3	1550 – 1650	225	Springs Heat treatable
'Platinum S + 2' (contains gallium)	19.5	1600 –1640/ 2910 – 2985	170 ann 290 aged	Heat treatable

Ann – annealed, c.w. – cold worked

Palladium: Palladium as a jewellery metal was only made hallmarkable in 2010. There is comparatively little information on the metallurgy and compositions of the new 950 palladium alloys on the market. Many are based on palladium-ruthenium, with other additions, including silver. Table 4 shows some typical commercial alloys. Ruthenium has a very limited solubility in palladium, so such alloys can be expected to be two-phase in structure. Hardness values mirror the equivalent platinum alloys, Table 3. On the other hand, the melting ranges of the 950 alloys tend to much lower. In Europe, there are lower fineness alloys at 585 and 500 on the market, with slightly higher hardness values compared to the 950 alloys and with lower densities and melting ranges.

Battaini has discussed development of 950 palladium-copper- and palladium-gallium- based alloys[39]; the gallium alloy showed most promise. This alloy contains 3.5% gallium, which is the limit of solid solubility, with small additions of copper, indium and aluminium too. It has an annealed hardness of 70HV, rising to 310HV after 70% cold work. It is assumed that this is a basically single phase alloy.

Very recently, Klotz and Held[40] have reported research on the development of new 950 palladium alloys for investment casting. These are based on Pd-5%Ru with additions of cobalt, tin and boron to widen the melting range, iron to reduce grain size and aluminium and boron to increase hardness. These alloys have good form-filling in casting, low reaction with crucible and mould investment and resistance to hot cracking.

Table 4 Typical palladium alloys on the market

Alloy (Supplier)	Fineness	Density, g/cm³	Main alloying metals	Hardness, HV	Melting range, °C
950 Pd (JM)	950 950	11.8	Ru Ru + Ga	120 (ac)	1350-1600
Tru-Pd (H&S)	950	11.8	Ga, Ag +	125 (ann)	1350-1380
Pd (W)	950 950 950 500 500	]12 – 12.5]]]11 – 11.5]	Ir Ru 4 Ru + 1Re 40 ?(Ag) 45 Ag+Cu	80 (ann) 130 (ann) 130 (ann) 130 (ann) 165 (ann)	1550-1650 Ditto Ditto 1150-1220 Ditto
Pd (H & M)	950 585 500	11.6 10.9 10.8	W + Ru 29Ag, + Ru +W 34Ag, + Ru + W	160 (ann) 170 (ann) 190 (ann)	1375-1465 1160-1245 1100-1180
Pd 950G Pd950G2 Pd750G Pd585 (L)	950 950 760 595	11.8 11.8 11.0 11.0	Ga, In Ru, Ga Ag, Cu 38Ag, Cu	103 (ann) 120 (ann) 164 (ann) 160 (ac)	1500-1550 1430-1480 1250-1300 1200-1250

Ann – annealed; ac – as cast;
JM – Johnson Matthey Plc; H&S – Hoover & Strong Inc; W – Wieland GmbH; H & M – Heimerle & Meule GmbH; L – Legor Srl;

THE PRESENT ERA – SOME RECENT DEVELOPMENTS

There have been a number of alloy developments launched on the market which are worth mentioning even though many have not yet achieved any significant commercial uptake. These are mostly gold-based alloys and include improved strength high carat golds and special surface and colour effects.

High strength high carat golds: As we have seen, high carat golds (24 ct, 22ct, 21 ct) are popular particularly in the Far East/ Middle East cultures. Such alloys tend to be soft single phase alloys and thus jewellery is prone to heavy wear and deformation. There is a desire for such alloys with improved strength and hardness. There have been two technologies developed in the last 30 years to meet this need, namely '990 gold' and micro-alloyed gold. These have been developed mainly for 24 ct gold jewellery but can be applied to the other high carat golds. The micro-alloying approach is also applicable to lower caratages and to silver, platinum and palladium.

The development of '990 gold' dates from the late 1980s[41,42]. It is a gold – 1% titanium alloy, i.e. 990 fineness, so is hallmarkable as 24 ct. It has mechanical properties considerably superior to 24 ct gold, approaching those of 18 ct golds, Table 5.

Table 5 Properties of '990 Gold'

	Annealed, 800°C, 1 h, WQ	Cold Worked, (23% reduction)	Age Hardened, 500°C, 1h, WQ*
Hardness, HV	70	120	170 - 240
0.2% Yield Strength, MPa	90	300	360 - 660
Tensile Strength, MPa	280	340	500 - 740
Ductility, % elongation	40	2 - 8	2 - 20

* range depends on whether aged in annealed, cold worked or aged and cold worked condition. WQ – water quenched

The basis for selection of titanium was the possibility of second phase precipitation as the alloy containing a 1% wt alloying addition in solution was cooled from 800°C to 400°C. From this, a table of probable hardening effectiveness was constructed, Table 6. The last column makes clear the reason for developing the 990 gold-titanium alloy. The promise of the rare earths and zirconium should also be noted.

Whilst this alloy has attractive properties, it has not found much commercial interest, probably because it requires relatively sophisticated alloying and manufacturing techniques in a market where cost is a priority and manufacturing capability has been unsophisticated. It was too advanced for its time!

In the early 2000s, a number of micro-alloyed golds were developed[43,44]. These are based on total alloying additions of 0.5 wt.% or less, typically 0.3% and even down to only 0.1 wt. %

in some instances, to effect a dramatic strengthening of the gold microstructure. Such small additions are approaching those typically used to control grain size. As gold is a low stacking fault metal (a type of crystal lattice defect), control of grain size alone or in combination with cold work will not yield significant hardening in pure gold, so such small additions cannot work through grain size control only. The basis is to add alloying metals with very limited solid solubility in gold, such that there is significant hardening by second phases; the metallurgy of such alloys has been described[43,44,45]. Typical alloying metals used include calcium and the light rare earths. Table 7 lists some of these micro-alloy developments (taken from reference 43).

Table 6 Candidate Alloy Systems and Probable Hardening Effect, taken from (41)

System	Solubility at 800°C	Solubility at 400°C	Fraction* wt%	Ratio, atom. wt.	Fraction* at%	Fraction harden. phase
Au - Ti	1.2	0.4	0.6	4.1	2.5	12.5
Au - Rh	0.6	0.2	0.4	1.9	0.8	0.8
Au - Ru	1.0	0	1.0	2.0	2.0	2.0
Au - Zr	2.0	0.3	0.7	2.2	1.5	7.5
Au - Tb	1.2	0.3	0.7	1.2	0.8	5.6
Au - Dy	1.9	0.3	0.7	1.2	0.8	5.6
Au - Ho	3.2	0.4	0.6	1.2	0.7	4.9
Au- Er	4.8	0.4	0.6	1.2	0.7	3.5

*Fraction of 1 wt % of alloying element precipitating at 400°C.

Again, some of these developments have been commercialised, notably in Japan but have not endured. The reason for this is probably the same as for '990 gold'. A particular problem here is that scrap materials cannot be simply remelted and recycled, as the micro-alloying metals oxidise away. This adversely impacts on the economics of such alloys.

Strengthening of high carat golds: Significant improvements to 22 ct golds have been described[46,47] using conventional alloying approaches. Van der Lingen and co-workers at Mintek and Fisher-Buehner of FEM have both demonstrated use of circa 2.0 - 2.5% cobalt and antimony additions to effect significant strengthening. Taylor[48] has also patented a cobalt-containing alloy, but with up to 1% boron included. However, as will be seen in reference 49, the microalloying approach can be effective in 22 ct and lower carat golds too, using gadolinium and calcium additions. Again, these stronger 22 ct gold alloys have not seen commercial uptake to date, despite strong market interest in the Indian markets.

Microalloying of Silver: In principle, it will be evident that the same approach for microalloyed gold could be applied to silver. The developer of PureGold (Table 7) has also developed PureSilver, a 99.3% silver micro-alloyed material and this is being marketed in the USA. It is claimed to be easy to work with as it does not require annealing, is very tarnish resistant, casts well and is harder than sterling silver. The patent[49] covers microalloyed gold, silver, palladium and platinum materials. In the case of silver, an alloy of at least 80.0% silver is claimed containing the rare earth gadolinium in the range 50 –15000 ppm, with optional

further additions of alkaline earth metals, silicon, aluminium and boron in the range 50 – 15,00 ppm in total, with hardness values of 130HV or higher and a Young's modulus of not less than 7,000 kg.mm^{-2}. These materials are claimed to be heat treatable. The use of gadolinium is claimed to be the most effective hardening element and results in a high Young's modulus. The small additions do not affect the colour.

Table 7. Improved Strength 24 ct Golds (compared to pure gold and 22 & 18ct yellow golds)

Material (Manufacturer)	Purity	Annealed Hardness HV	Cold Worked Hardness, HV	Strength MPa	Ductility %	Comments
High Strength Pure Gold (Mitsubish, Japan)	99.9%	55	123	500	2	Castable
TH Gold (Tokuriki Honten, Japan)	99.9%	35 - 40	90 - 100	-	-	Castable
Hard 24 Carat (Mintek, S Africa)	99.5%	32	100 Aged: 131 - 142	-	-	Age Hardenable
PureGold (Three O Co, Japan)	99.7%	63	106 Aged: 145-176	-	-	Castable, Hardenable, Chain
Uno-A-Erre 24ct Gold (Uno-A-Erre, Italy)	(i) 99.6% (ii) 99.8%	33 62	87 118	-	-	Both used in c.w. condition
DiAurum 24 (Titan, UK)	99.7%	60 (as cast)	95	-	-	Castable
Pure Gold	*99.9*	*30*	*50*	*190 -380*	*Ann: 40 C.W.:1*	
22 ct Yellow (5.5 Ag - 2.8 Cu)	*91.7%*	*52*	*100 - 138*	*220 -440*	*Ann: 27 C.W.: 3*	*Castable*
18 ct Yellow (12.5 Ag - 12.5 Cu)	*75.0%*	*150*	*190 - 225 Aged: 230*	*520- 900*	*Ann: 40 C.W:. 3 Aged: 15*	*Castable, Age Hardenable*

Microalloying of Platinum: Microalloying of platinum should also be possible. Of course, oxide dispersion strengthened platinum (such as ZGS platinum from Johnson Matthey) for industrial applications has been on the market for many years, but has not found interest in the jewellery sector.

In a patent from Japan, a hard, high purity platinum alloy containing 10 –100 ppm of cerium is claimed[50], that has a good hardness, lustre and tarnish resistance suitable for jewellery manufacture and is at least 99% purity. Vacuum or inert gas is required during melting to prevent loss of cerium by oxidation. The platinum-cerium phase diagram shows characteristics similar to that of the gold-cerium system[43,44], i.e little solid solubility of Ce in

Pt, a eutectic system between Pt and a high platinum-containing intermetallic. For cerium contents of 0.03 – 0.3%, hardness values of 61 – 102HV were obtained compared to 40HV for pure platinum and 120 –136HV for 950 fineness platinum alloys.

A commercial platinum, HPP Platinum, from Johnson Matthey is claimed to have improved strength and contains about 250ppm of samarium, at 999 fineness[34]. A hardness of HV55 compared to HV 50 for a pure 999 platinum is published. Work by Ning at the Chinese Institute of Precious Metals on rare earth additions has shown that rare earth additions to platinum can improve strength [see references 3 - 5 in (51)]., Ning and Hu show that a 0.05% cerium addition to a platinum – 15% palladium-3.5% rhodium alloy increases room temperature tensile strength from 280 MPa to 400Mpa, with similar improvements to tensile and creep strength at 900°C. These increases are attributed to both solid solubility and dispersion strengthening effects.

The Ogasa patent[49] also includes platinum materials. This claims platinum alloys of at least 85.0% platinum containing gadolinium and the other optional elements, preferably calcium, in the range 50 – 15,00ppm in total. Cast hardness values of at least 120HV and Young's modulus of not less than 8,000 kg.mm^{-2} are claimed. With 50% cold work, hardnesses of at least 150HV are claimed.

Thus, in summary, it is evident that microalloyed platinum alloys are possible, although it not clear whether they are being commercially produced for jewellery application, and that rare earths and calcium are preferred micro-alloying additions, paralleling the work on gold.

Alternative White golds: The advent of the EU Nickel Directive that limits use of nickel in jewellery and the higher cost and density of palladium has resulted in much R & D to find alternative white alloys. Alloying additions of manganese, iron and chromium for example have been evaluated [see for example references 52, 53, 54, 55 and references therein], but have been found wanting on important aspects, such as a tendency to crack or tarnish heavily. Basso et al have explored the use of gallium[53] and, recently, Peretti et al have explored the use of germanium as a whitener[54].

An interesting development has been reported by Simonet[55]. She reports the development of a very white alloy (it has a very low Yellowness Index of 7) that is suited to manufacture by Selective Laser Melting (3D printing/additive manufacturing). Thus, the alloy is only required in powder form and so some constraints imposed by conventional processes are removed. This gives some extra freedom in terms of alloy design. The alloy is an 18ct gold - 15% chromium – palladium-iron composition. It has a lower density of 13.5 g/cm^2 compared to a 15% palladium white gold, which gives an economic benefit, and is resistant to tarnishing and corrosion. It has a good hardness of 215HV rising to 480+HV in the age hardened condition, indicating good wear and scratch resistance, and high yield and tensile stresses whilst retaining good ductility.

Unusual colours: There has long been an interest in unusual colours of precious metals. Some of these are intrinsic to the alloy and are based on coloured intermetallic precious metal compounds and others are achieved by surface treatments and coatings. Gold has received the most attention and so colours such as purple, blue, black and brown can be made. The topic has been reviewed[56,57]. Some commercial success has been achieved, notably purple gold, applied as a coating of the gold-aluminium intermetallic $AuAl_2$, and blue, black and brown, generally applied as an oxidation of the alloy, tailored in composition with additions such as cobalt. Some coloured intermetallic compounds of platinum and gold have been used to form pseudo gem stones, marketed under the 'Platigem' label, but have not achieved commercial success.

Unusual surface textures: Intermetallic alloys in the gold-aluminium-copper system show a quasi-martensitic transformation which results in a colourful sparkle effect on the surface. Marketed under the label 'Spangold', they are developed at 18 and 23 ct gold content[58,59] but have not found commercial interest.

THE FUTURE

It is evident from the foregoing that precious metal jewellery alloys have become more complex and precise in composition to optimise properties to meet manufacturing and market needs. We note that over the last century, alloy compositions are being tailored to suit manufacturing processes, to obtain improved performance in service with the consumer and to meet the latest market and legislative demands in terms of quality, health & safety and appearance. Cadmium and nickel are good examples of metals now limited or banned and this has led to new alloy developments, including cadmium-free solders. The irritation of firestain and tarnishing has led to improved silver alloys and the problems in casting, particularly the incidence of porosity, has recently led to the development of improved platinum casting alloys, although these are yet to see commercial application.

New manufacturing technologies also impacts on alloy development. More recently, the advent of selective laser melting of precious metal alloy powders to produce net-shape jewellery has shown that alloys need to be tailored to the process. High vapour pressure metals such as zinc are not desirable constituents of alloy powders. The new very white gold alloy[55] has been enabled by this new process. It has a relatively low thermal conductivity compared to conventional carat golds which, with the lower reflectivity of the alloying elements, results in more efficient melting of the powders during laser heating. Others have also noted that alloy compositions need to be changed for selective laser melting, for example in sterling silver to facilitate better consolidation (reduced porosity) of the alloy[60] and the use of additions of germanium and iron to lower thermal conductivity and reflectivity in 18 ct yellow gold has been demonstrated by Klotz[61].

Alloy development is also in a new phase. No longer is the old 'trial and error' approach appropriate for a rapid development of improved alloys, even if conducted in a structured way. The new 'alloys-by-design' approach uses algorithms based on the latest science, proprietary software, and computing horsepower to predict the performance of millions of different alloys simultaneously, and choose the best optimisation for a particular application[62]. This approach starts with a lot of basic data on various properties and alloying behaviour which is fed into scientific computer models and allows the modelling of performance of different compositions and hence optimisation of composition to suit the application requirements. It will be interesting to see how this approach impacts on improved jewellery alloys. Obvious applications would be improved strength 22 ct and other high carat gold alloys and improved strength sterling silver alloys with firestain and tarnish resistance.

There are two areas of novel precious metal alloy development that are at an early stage in terms of R & D and have yet to be exploited commercially in the jewellery industry. These are (i) Bulk Metallic Glasses, otherwise known as amorphous metals and (ii) Shape Memory Alloys (SMAs). This may be due to the industry being unsure of what benefits such alloys could bring to jewellery and their manufacture.

Bulk Metallic Glasses (BMGs): These are alloys that do not solidify into a normal crystalline structure but to an amorphous structure. The alloy compositions are close to deep eutectic compositions and solidification to the amorphous structure requires rapid cooling conditions. This amorphous or glassy state is metastable at ambient temperatures and the alloy will crystallise above a critical temperature. The interest in such alloys lies in their

unusual properties such as high strength and hardness , large elastic strain limit, near zero shrinkage on solidification and good processing capability, namely casting and thermoplastic-type deformation which enables substantial forming to complex shapes

The first alloy found to exhibit metallic glass formation was the gold-silicon eutectic. Such gold eutectic alloys have a critical cooling rate of the order of 10^6 °K/s and this translates into a critical casting thickness of about 50µm. Since this discovery, a number of precious metal alloys, gold- , palladium – and platinum- based have been developed[63] . In particular, two alloys suitable for jewellery application have been developed by Lohwongwatana and colleagues[64]. One is an 18 ct gold alloy of composition gold 76.26% - silver 4.69% - palladium 1.93% - copper 13.5% - silicon 3.62% and the other is an 850 finenesss platinum alloy of composition platinum 85.24% - copper 7.3% - nickel 2.36% - phosphorus 5.3% . These alloys have a critical casting thickness of 5mm and 20mm respectively. In terms of properties, they have low melting temperatures (371°C and 522°C respectively), can be worked at low temperatures and have high yield strength of 1100MPa and 1470MPa respectively with high hardness values of 360HV and 400HV as cast. Alloy densities are also markedly lower. In terms of processing these alloys, a schematic TTT diagram is shown in Figure 4. Curve 1 is the cooling curve necessary to avoid crystallisation during casting (curve 2 would result in crystallisation). Curve 3 is where the feedstock material is reheated into the supercooled liquid regime to enable thermoplastic forming , i.e. it behaves like a thermoplastic.
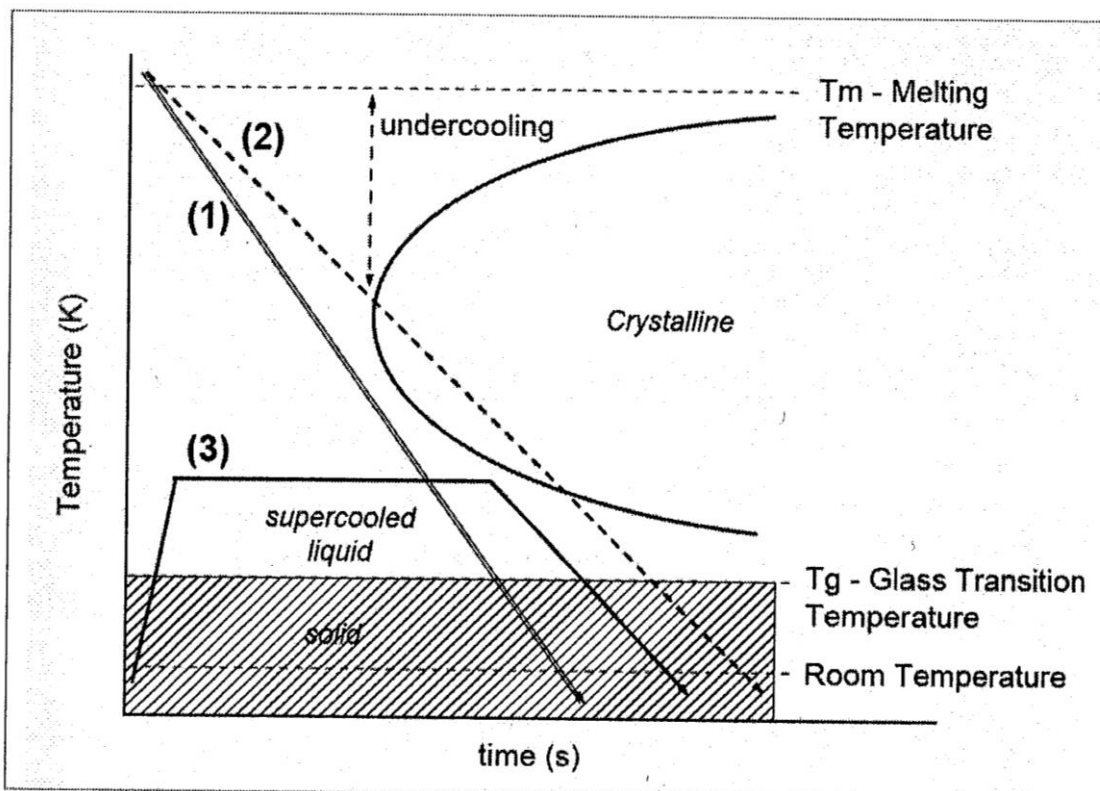

Figure 4. Schematic Time-Temperature-Transformation diagram for Bulk Metallic Glass alloys [from reference 64]

Figure 5 shows an example of the net-shape formability of the gold BMG using thermoplastic forming (left) and for the platinum BMG (right), along with some particulate feedstock material. The casting of jewellery items in gold BMG alloys has been studied by Klotz &

Eisenbart[65]. They showed gold BMGs can be cast into complex shaped jewellery products. They also showed such alloys have a good white colour, but a drawback was that the alloys tarnished rapidly. Clearly, there is scope for further alloy development to overcome this problem. To date there has been some application of these materials in the watch industry.

Shape Memory Alloys (SMAs): These are a class of alloys that can be heavily deformed in shape, but when heated above a critical temperature, return to their original shape. They also exhibit superelasticity, i.e. large elastic strains when deformed above the critical temperature. Many SMAs are intermetallic compounds[63] and gold-based SMAs have been discovered, e.g. ternary gold-copper-zinc alloys and gold-nickel -titanium alloys where some gold replaces nickel in the well known nickel-titanium alloy, Nitinol[66]. Such gold SMAs have some drawbacks such as poor cold deformability. There is scope for more alloy development to produce better alloys. A problem is how can one use the shape memory properties effectively in jewellery design and manufacture. Use for mounting gemstones has been suggested and the possibility of using them to join components together (as Nitinol was originally used for) must also be considered. Platinum-based SMAs have also been researched[67,68] This could be an interesting field for further R & D to develop better precious metal SMAs and explore their potential for jewellery application. We are in an era of smart materials and there may be a niche here for SMAs for use in smart jewellery.

Figure 5. Gold BMG (left) and 850 platinum BMG (right) boxes , both formed by thermoplastic process; also some BMG bead feedstock (from reference 64)

CONCLUDING REMARKS

In this presentation I have explored the development of precious metal alloys for jewellery application through history to the present day, with some comments on possible future developments. Our industry has been inherently conservative in outlook with regard to use of new technology, but there is no doubt that jewellery alloys have become more sophisticated over time and tailored to particular manufacturing processes and improved consumer performance. We have seen alloys tailored for better castability in the investment (lost wax) casting process, for improved tarnish resistance, for easier wrought fabrication and now for better use in selective laser melting (otherwise known as 3D printing) to produce net-shape components. Here a major requirement has been to lower reflectivity and thermal conductivity to enable a more efficient heating and melting. I have not discussed the advances in deoxidation in melting and casting or the use of grain refiners to produce better,

more ductile alloys for manufacture that we now take for granted. Our understanding of deleterious additions/impurities is also greatly advanced.

I have also attempted to look into the future. In current applications in jewellery, there is still a need for improved alloys with better consumer performance such as stronger alloys, and improved tarnish resistance. Possible new alloy developments such as bulk metallic glasses and shape memory alloys need further exploration too. It is also likely that future health and safety legislation may impose more constraints on alloy compositions and stimulate further alloy development, as we have seen with nickel in white golds and cadmium in solders. Market demands may also have an effect, for example a wider palette of colours or special surface effects.

We are also in an era where ethical sourcing of raw materials, sustainability and responsible manufacturing has become increasingly important. Corporate social responsibility is a significant factor today. How this will impact the jewellery industry in the future is not yet clear. Whether it will affect the jewellery alloys of the future is a question difficult to answer. Some alloying metals used in jewellery alloys may become scarce and expensive. All I can say is that the industry will respond to such pressures and that will include better precious metal alloys in jewellery. Maybe we will see other precious metals, for example those in the platinum group, becoming popular in jewellery. Maybe we will see composites of precious metals and other materials emerging such as deformation processed precious metal matrix composites (DMMCs)[69]. There will be change, of that I am sure! Thank you.

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