

White Golds – Meeting the Demands of International Legislation

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In the current fashion wave for white metals, white gold jewellery is proving popular in many major markets and this gives rise to many export opportunities for producers. However, with current and imminent national legislation against the use of nickel and technical problems that arise in manufacturing certain white golds, many manufacturers are confused. This presentation reviews the metallurgy and processing of white golds and the possible options for commercial alloy compositions suited to the production of jewellery against the background of the nickel legislation.

18ct white golds were originally developed in the 1920's as a substitute for platinum alloys. There are a number of elements that will bleach gold white but the major ones used today are nickel and palladium for the high carat alloys and, additionally, silver at the low carats. There have been a number of excellent articles and reviews on White Golds, notably by McDonald and Sistare (1) on nickel white golds, Susz (2, 3) on palladium alloys, Normandeau (4, 5) on compromises in performance and O'Connor (6) on alloy requirements and characterisation.

Nickel Sensitivity is obviously the major issue we are faced with at the moment. It has been reported that between 10 – 15% of women and 2% of men have an allergic skin reaction to nickel - containing alloys. Once sensitised, the wearer may then develop reactions elsewhere on their body. Therefore, to protect consumers, some European countries have already brought in legislation against the use of nickel in contact with the skin and the E.U. has now drafted legislation that will prohibit or restrict the use of Nickel in all products. The legislation is known by

the title "*The Nickel Directive*". USA may possibly follow and Japan is operating a voluntary system.

The Nickel Directive

The European "Nickel Directive" was published in July 1999. This will make its component standards mandatory – i.e. law – for all products, either manufactured or imported into the member states from January 2000.

The directive states that nickel may not be used in the following :-

1. In post assemblies, which are inserted into ears and other parts of the human body that are pierced, during epithalisation (healing) of the wound caused by piercing, whether subsequently removed or not, unless such assemblies are homogeneous and the concentration of nickel – expressed as mass of nickel to total mass – is less than 0.05%.
2. In products intended to come into direct and prolonged contact with the skin if the rate of nickel release is greater than exceed 0.5 $\mu\text{g}/\text{cm}^2/\text{week}$. These products include earrings, necklaces, bracelets, chains, anklets, finger rings, wrist watch cases, watch straps and tighteners.
3. In products and applications such as those outlined in section 2, where these have a non-nickel coating, unless such coating is sufficient to ensure that the rate of nickel release from those parts will not exceed 0.5 $\mu\text{g}/\text{cm}^2/\text{week}$ for a period of at least two years of normal use of the product – this is determined by putting items through a simulated 2 year wear cycle.

Note: all of the above standards will be available from any European Standards Office once published.

The following points relate to nickel white golds :

- Section 1 generally rules out all nickel-white carat golds for this purpose. Epithalisation is understood to mean "healing" but there are no guidelines on how to determine when epithalisation is complete or whether this also includes piercings damaged after initial healing has been completed. There is still some debate as to what the definition of a "post assembly" is and whether the front and back surfaces of an earring adjacent to the post are also included in this part of the directive. Unless you are confident on your interpretation of the Directive, the general rule of thumb must be "if in doubt – leave it out".
 - Section 2 is also open to interpretation when considering release rate test results. Determination of the surface area of an item may be complex and result in differences in the calculated release rates for identical items depending on the surface area calculation – how would the surface area of a link-type watch strap be determined? One manufacturer has tested all their nickel-containing alloys to this standard and found all to comfortably pass the release rate test, even with nickel contents of up to 12%.
 - Section 3 only applies here if a nickel-containing white gold is used and then plated with rhodium or some other element. Presence of the rhodium plate will not exclude the item from the release rate test and it must undergo the simulated 2 year wear cycle prior to release rate testing.
- The Directive was published in the European Official Journal in July 1999, and member states are allowed six months to implement the Directive as national law.

Table 1. Requirements for an ideal 18 carat white gold jewellery alloy

Principal Requirements	Known Restrictions	Secondary Requirements	Known Restrictions
Good colour and reflectivity	Low Copper	Easy to braze or solder	
Hardness < 200 HV and preferably 120 to 150 HV	Limited Nickel	Amenable to electroplating or electropolishing	
Adequate cold workability, elongation > = 25%	Limited Zinc	Resistant to fire cracking	
Liquidus temperature < = 1100 °C	No refractory Metals	Simple to recycle	No reactive or volatile metals
Suitable for casting	No volatile metals (for vacuum casting)	Easy to polish	
Competitive cost	No platinum group metals	Low susceptibility to tarnish and corrosion	

extent. Nickel and palladium are 2 primary metals that will bleach gold white in the high carat alloys (14/18ct), whilst at low carat alloys (8/9/10ct), silver is also used to bleach gold. Other elements will bleach gold, but not to the same degree as palladium or nickel. These other alloys often do not possess suitable physical or mechanical properties.

Alloy Requirements

O'Connor (6) has detailed the primary and secondary requirements for white gold alloys. These are shown in Table 1. It is difficult to attain all these requirements in one single alloy and often compromises have to be endured.

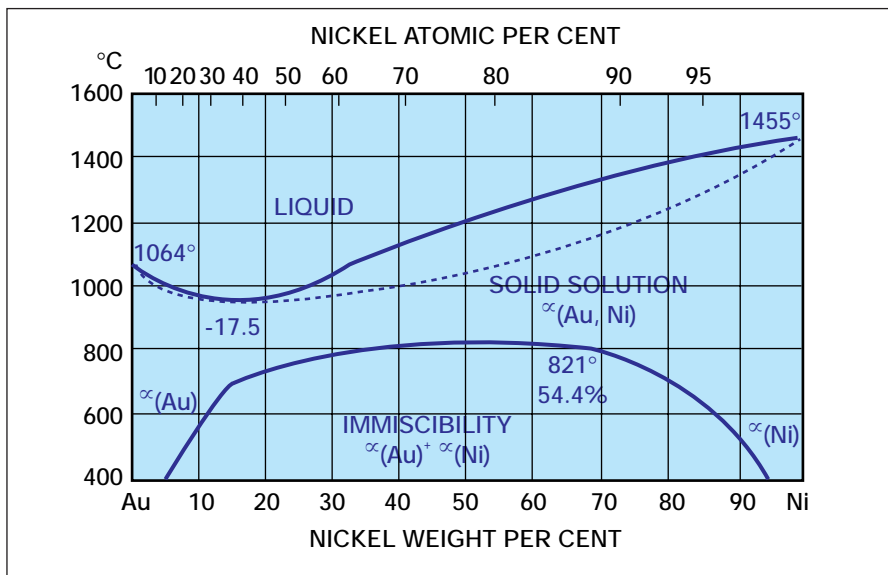


Figure 1 – Gold Nickel Phase Diagram

Manufacturers, Importers and Importing Wholesalers then have six months to ensure all relevant products comply with the directive, after which it will be illegal to sell non-conforming product.

Wholesalers and Retailers will then have a final twelve months to clear any non-conforming stocks, again after which it will be illegal to sell non-conforming product.

Non-compliance with the Directive is a criminal offence, punishable by fines and/or imprisonment. As already stated, the Directive will also

apply to items imported into the member states. It is possible that importers will require accredited certification as proof of conformance to the Directive.

White Gold Alloys

18ct white golds were originally developed as a cheaper substitute for platinum alloys. Gold and copper are the only 2 pure metals which are coloured. All other metals are white or grey in colour. Additions of other metals will, therefore, tend to bleach gold white to a greater or lesser

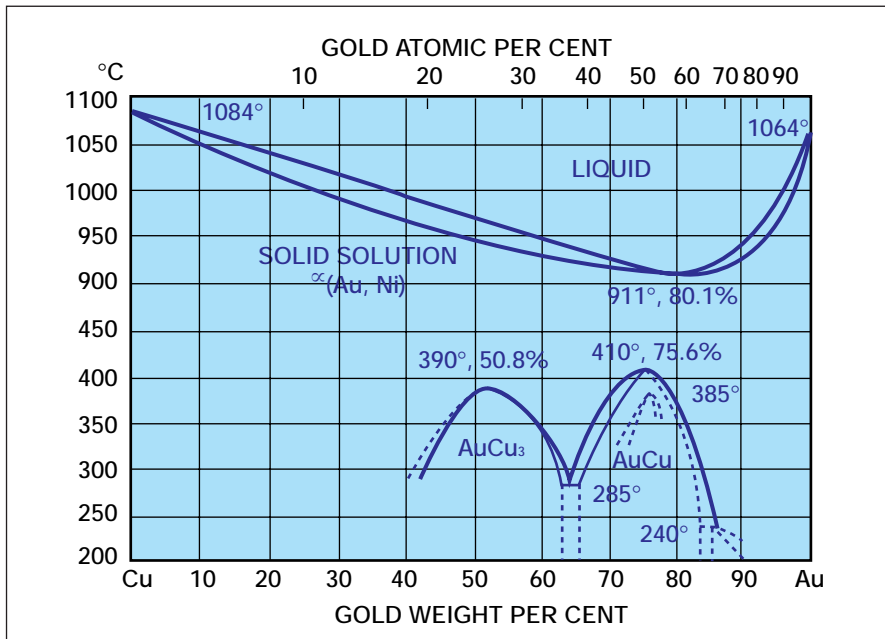


Figure 2 – Copper – Gold Phase Diagram

Nickel White Gold Alloys

These benefit from low cost, a liquidus temperature below 1100°C, which allows them to be cast relatively easily, and they have a good colour but with a cold steely appearance. It is difficult to combine good colour and workability.

The metallurgy this alloy system has been reviewed by McDonald and Sistare (1). These alloys are based on the gold-copper-nickel system with additions of zinc and/or palladium. The metallurgical behaviour is determined by the gold - nickel and gold - copper binary alloy systems.

In the solid state, the gold-nickel system, Figure 2, is characterised by a continuous solid solution at high temperatures with a miscibility gap at low temperatures. The solid solution decomposes into 2 phases, one gold-rich and the other nickel-rich. This decomposition increases the hardness of the alloys and they become difficult to process. High nickel alloys have high hardness and work hardening rates and, therefore, need frequent annealing. Conversely, low nickel alloys have poor colour but good workability. There are also problems with poor corrosion resistance of the nickel - rich phase.

Copper is added to nickel white gold to improve the workability of the alloys. The main feature of the gold - copper system, Figure 2, is the

ordering reaction that takes place. The hard, intermetallic AuCu phase is formed at approximately 400°C and leads to an increase in hardness. The addition of copper is a question of compromise between colour and ductility. Large additions of copper reduce the whitening effect of the nickel but improve the workability of the alloy. Alloys with small additions have a good colour but are difficult to work. In Figure 3, it can be seen the miscibility gap extends over a large portion of the ternary gold-nickel-copper system.

Zinc is added as a secondary whitener to these alloys to compensate for the colouring effect of copper and enhance the whitening effect of the nickel. It also acts as a deoxidant during investment casting and promotes the wetting of the investment used in this process. Zinc

Table 2. Typical Nickel White Golds

	Au %	Cu %	Ni %	Zn %	Hardness Hv	Liquidus °C
18ct	75	2.2	17.3	5.5	220	960
	75	8.5	13.5	3.0	200	995
	75	13.0	8.5	3.5	150	950
14ct	58.5	22.0	12.0	7.4	150	995
10ct	41.7	32.8	17.1	8.4	145	1085
9ct	37.5	40.0	10.5	12.0	130	1040

additions tend to be restricted as the alloys are susceptible to fire cracking during annealing. Volatilisation of the zinc occurs during melting and may create further problems with scrap re-use and loss in ductility.

Processing of nickel white golds requires a >50% reduction in area between anneals. Small or uneven reductions in area should be avoided. Following annealing, the alloys should be air-cooled to black heat and then water quenched.

Nickel white golds are used in all the standard carats from 8 to 18ct. Typical formulations are shown in Table 2. It can be seen that, as the caratage is reduced, then larger additions of copper and zinc are required to maintain the alloy properties.

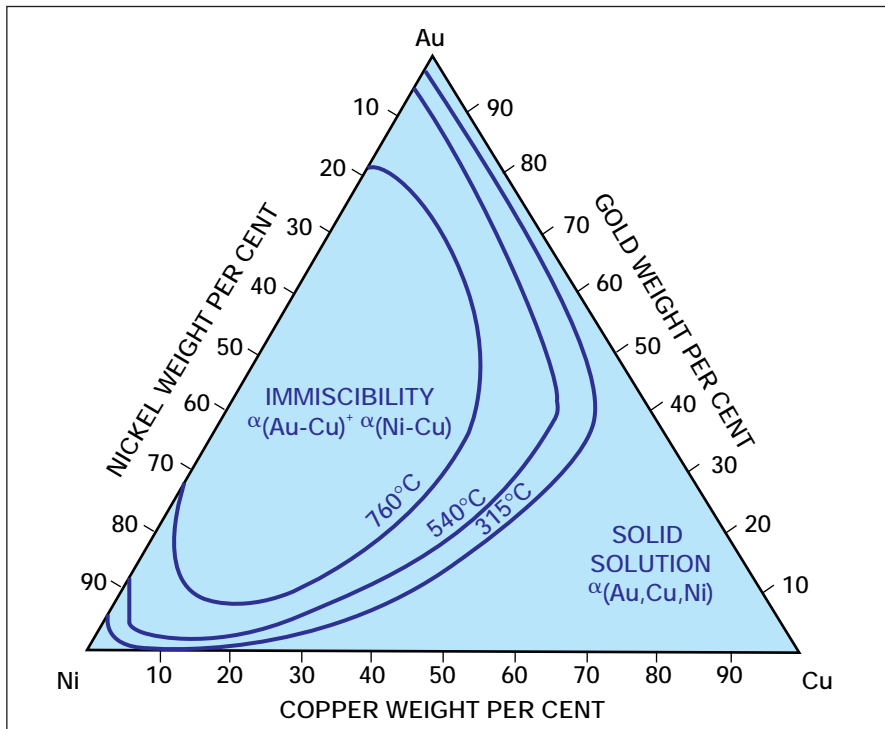


Figure 3 – Projection on the room temperature plane of the Gold-Copper-Nickel Ternary Phase Diagram

Alternative White Gold Alloys

Additions of other metals, which are all white/grey in colour, will tend to bleach gold white to a greater or lesser extent. Nickel as has been discussed is one of the primary bleachers of gold and palladium (and platinum) is the other major metal that will bleach gold well. Other metals that have been proposed or used include silver, which is a moderate bleacher, zinc, manganese, iron, indium and cobalt. These are the principle secondary bleachers of gold.

Palladium White Golds

These alloys have an attractive warm grey-white colour. They have low hardness and are soft and easy worked. Their mechanical properties vary smoothly with composition and they possess excellent corrosion resistance. However, due to the current high price of palladium, they are expensive and because of their high density, jewellery weighs more and also contains more gold. They also have high melting temperatures (>1100°C). This can make them more difficult to process during melting.

The majority of these alloys are based on the gold-palladium-silver system, which has been reviewed by

Susz (3) and Normandeau (4). They are blended with copper, zinc and nickel to give the requisite mechanical and physical properties. They are becoming increasingly used in Europe as a replacement for nickel white golds. It should be noted that some palladium white golds are not nickel-free.

The metallurgical behaviour is determined by the characteristics of the binary alloy systems, Figures 4, 5 & 6. These alloy systems show complete miscibility in all concentrations i.e. they are all single phase. As a consequence, they do not

Table 3. Typical Palladium-Silver Alloys

	Au %	Pd %	Ag %	Cu %	Zn %	Ni %	Hardnes Hv	Liquidus °C
18ct	75	20	5				100	1350
	75	15	10				100	1300
	75	10	15				80	1250
	75	10	10.5	3.5	0.1	0.9	95	1150
	75	6.4	9.9	5.1	3.5	1.1	140	1040
	75	15		3.0		7.0	180	1150
14ct	58.3	20	6	14.5	1		160	1095
	58.5	5	32.5	3	1		100	1100
10ct	41.7	28	8.4	20.5	1.4		160	1095
9ct	37.5		52	4.9	4.2	1.4	85	940

exhibit problems with segregation and hardening due to precipitation.

10 – 12 % palladium is needed in 18ct white golds to produce a good white colour. Typical formulations in the gold-palladium-silver system are shown in Table 3.

Blended White Golds

It can be seen from Table 3 that some palladium alloy formulations contain nickel. Similarly, some nickel white gold alloys contain palladium. Palladium white golds, therefore, are not necessarily nickel-free. In fact, a large number of alloys used today contain both nickel and palladium. They are blended white golds. 18ct palladium-based alloys with low nickel contents often meet the requirements of the “Nickel release test” but cannot be classified as “nickel-free”.

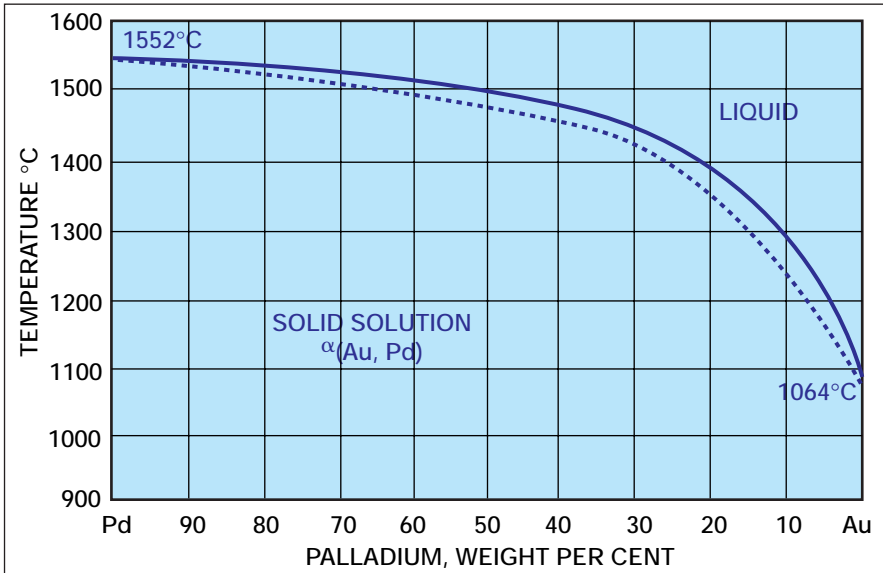


Figure 4 – Gold – Palladium Binary Relationship

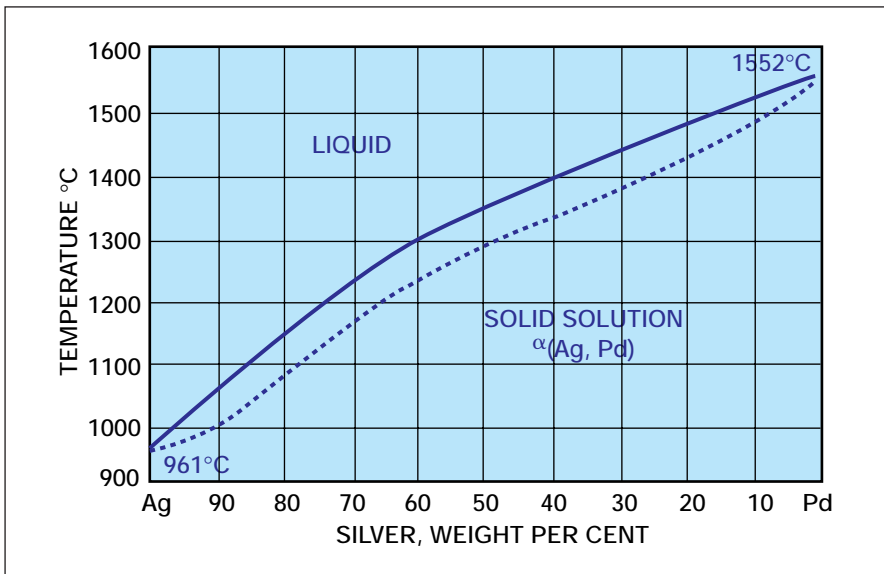


Figure 5 – Silver – Palladium Binary Relationship

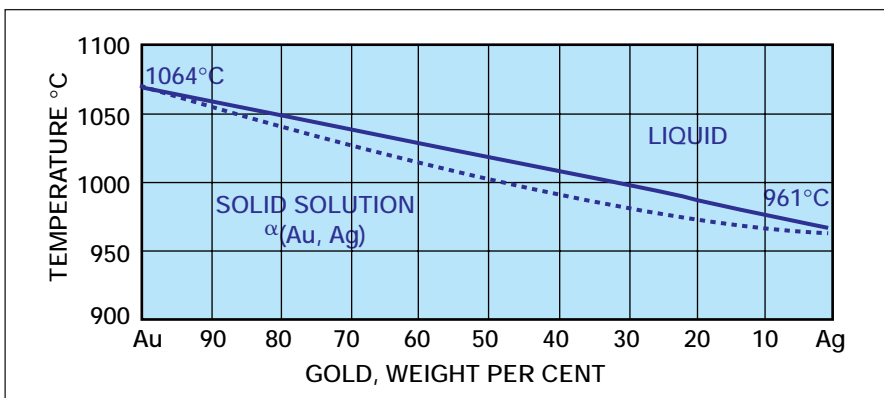


Figure 6 – Gold – Silver Binary Relationship

Silver White Golds

At low carat levels (8/9/10ct golds, silver in high concentrations is used as a bleach and provides alloys that have a good colour, Figure 7, and are soft and ductile. Palladium, copper, zinc and nickel are added to improve the alloy properties. The alloys will only tolerate small amounts of copper and zinc before their colour is impaired. These alloys behave similarly to sterling silver (92.5% Ag) in that they have poor corrosion resistance and react with sulphur in the atmosphere, as does Sterling Silver, to form a tarnish film.

Other White Golds

Over the last 30 years, concerted efforts have been made to replace nickel and palladium as the primary whiteners of gold. A large range of other elements have been looked at as secondary whiteners

In a large research project over 20 years ago, one company surveyed over 103 elements of the periodic table and rejected all but 12 as having possibilities. They then examined more than 60 different alloys with little success, the majority of these being rejected for poor colour and/or workability. Similarly, MacCormack and Bowers (7) examined 206 compositions looking at the effects of secondary whiteners in palladium or nickel alloys with only limited success.

At best to date, 5 possible alloy systems have shown some promise. These include platinum, iron, manganese and indium. Research is still continuing, but there are considerable problems to overcome.

Platinum is a good whitener of gold. For many years it has been used in the Dental industry in alloy formulations, often with palladium. The alloys are white, are often hard or are hardened by precipitation for service requirements. In Japan currently, white gold jewellery is selling well and is taking a share of the dominant platinum jewellery market for white precious metal. An 18ct alloy containing 10% platinum, 10% palladium, 3% copper, 2% zinc offers a suitable range of desired properties for use in jewellery and it is having some success in the market given its price differential with platinum.

The use of iron has been studied and may find a role as a secondary whitener but large amounts of palladium are still needed to maintain the colour and workability of the alloys, particularly at lower carats (14ct). The gold-iron system is also 2 phase, which may lead to possible hardness problems and a susceptibility to corrosion.

Indium in small amounts, ca 2 to 3%, is used as an auxiliary bleach for gold, again in conjunction with palladium. It has the benefit of being a low melting point metal and helps to reduce the high melting ranges of the palladium alloys. Alloys with high levels of indium are hard and difficult to work. Increasing the indium content in a 18ct palladium alloy from 2.5 to 7.5% reduces the ductility (measured as %elongation) from 30% to 5%.

The use of manganese as a whitener for gold alloys has long been known though very few alloys have been commercialised to date. It offers the best potential for development of new alloys, although they will probably still need to be combined with a minimum of 5% palladium, preferably 10% palladium, to provide suitable alloys (8). The alloys are soft and white. They can suffer problems with corrosion resistance due to with the formation of a highly tenacious oxide. High manganese-containing alloys are somewhat brittle, they are

susceptible to stress corrosion cracking and react with carbon used in casting crucibles.

Colour

There are currently no agreed international standards for the colour of gold alloys. Obviously, this can and does lead to problems between the supplier and customer over colour. However, colour is now generally measured using the CIELAB system in which a spectrophotometer measures 3 polar co-ordinates L, a, and b which then gives a direct measurement of the samples chroma, C (7)

This system is useful only for large flat surfaces and as such has not been developed sufficiently to enable direct measurement of jewellery items, which by their nature have complex forms.

As we have shown previously the colour of white gold alloys is often compromised by the metallurgical and working behaviour of the alloys. Both low nickel and low palladium containing alloys have a yellowish brown colour and such alloys are normally electroplated with rhodium (a platinum group metal) and have an excellent white colour. If sufficient rhodium is provided, then the piece of jewellery should stay white for a number of years before the underlying yellow-brown of the gold alloy shows through. The articles of jewellery may then be re-plated with rhodium. Rhodium plating can cause problems with sizing of rings. It needs to be removed before the ring can be sized and then re-plated, thus adding cost to the process.

White Gold Solders (Brazing Alloys)

The main commercial white gold solders on the market today are based on nickel as the primary bleaching agent. They often have concessionary gold contents for hallmarking purposes – typically 83.3%, 58.0% and 50.0% gold to enable step soldering. As jewellery solders tend to be operated within the range of 650 – 850 C, palladium, with its high melting point, tends to increase the melting range of the solders, making them impracticable and is therefore generally not used. Other low melting point metals such

as zinc, indium, gallium and cadmium, plus silver and/or copper as an additional metal, are also used in solder alloys and manganese with levels of 3-5% may give opportunities for nickel-free alloys for the jeweller (8).

Investment Casting of White Golds

It is worthwhile looking at the investment casting of white golds as large quantities of jewellery are produced using this process. Nickel based alloys can react with gypsum-bonded investment, giving a rough surface and often, gas porosity due to sulphur dioxide formation. Similarly, palladium alloys, due to their high melting points, react and degrade the investment.

The major elemental components of these alloys are silver, copper and zinc. These additions are made to impart improvements to the alloy properties, i.e. strength, but they can have a considerable effect on casting performance due to their reaction with gypsum investments and the casting atmosphere.

Normandeau has studied metal/mould reactions (9) on 14ct nickel and palladium white golds. The incidence of reaction was greater with the nickel white golds. With the nickel white gold, he observed extensive damage due to sulphur dioxide gas formation. He proposed that the zinc in the alloy reacted with the gypsum to generate sulphur dioxide. In the palladium alloy it appeared that the silver present in the alloy combined with the sulphur from the decomposition of the investment to form silver sulphide. This appears as a protective smooth surface layer on the casting and further protects against the reaction with the investment. This surface layer, though, is hard and difficult to file during the finishing operation.

Copper has a tendency to oxidise if it is not well protected by a suitable gas cover such as argon. The oxides often appear as inclusions during polishing and are distributed throughout the casting. They impair the finish of the product. Zinc will protect against oxidation of the copper but it easily volatilises at high temperature and tends to coat equipment in a layer of zinc or zinc oxide, leading to cross-contamination of future melts.

The introduction of vacuum casting equipment has seen an improvement in the quality of castings. Induction heating, with good power control and accurate temperature measurement, has helped to improve the reproducibility of the process. Vacuum melting and

casting allows the alloys to be processed in oxygen-free atmospheres, thus removing the major problem of copper oxidation.

Recent developments in higher temperature gypsum-based investments which can operate successfully up to 1200°C are now allowing the high temperature, high palladium white gold alloys to be successfully cast. Previously, these alloys reacted with the traditional gypsum-bonded investment giving poor quality castings. This required the use of phosphate-bonded investment, normally used for the casting of platinum alloys.

Conclusions

There are numerous white gold alloys available to the jeweller, the choice of which depends on budget and use. There are commercially available nickel-white alloys that do not require rhodium plating and are inexpensive compared to the palladium-bearing alternatives; however, they can be difficult to process and do not comply with parts of the European Nickel Directive, indicating restricted use. Alloys with lower nickel contents, which also fall into this category, are generally easier to process but will require rhodium plating.

The palladium-white alloys will conform to the Nickel Directive. However, the types of alloy available vary greatly with use and cost – the price of palladium at present has a significant effect on the intrinsic cost of an alloy. There are excellent alloys commercially available with higher

palladium contents, which do not require final rhodium plating and have excellent tarnish resistance. However, these may be of limited use depending on the process used: investment casting can present some problems with the higher melting range alloys. The lower content palladium alloys are, by definition, less expensive but will generally require final rhodium plating.

Although all types of alloys discussed have both advantages and disadvantages, the one certain thing is the customer has a wide range of choice for whatever process is required.

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