# Production and characterisation of 18 carat white gold alloys conforming to European Directive 94/27 CE

**M. DABALÀ*, M. MAGRINI*, M. POLIERO**, R. GALVANI***
**D.I.M.E.G., University of Padova, 35131 Padova, Italy*
*** Leg.Or., Bressanvido, Vicenza, Italy*

## Summary

White gold alloys were developed to substitute platinum in jewellery applications. The Au-Ag-Cu system cannot be used to produce white alloys because of yellowing in high carat alloys and tarnishing in low carat alloys. Moreover, use of nickel for whitening gold alloys is discouraged due to the potentially allergenic effect of this element. The European Community has recently issued a Directive to limit nickel content in jewellery in contact with the skin. In this paper, the preparation of 18ct. white gold alloys, either nickel-free or of low nickel content, is described and their melting range, microhardness, colour and metal release characteristics measured.

## Introduction

Historically, white gold was sought and discovered by goldsmiths who required a cheaper alternative to platinum in jewellery. Platinum was expensive to produce and difficult to cast and cold work. From its earliest production, white gold alloys were made by alloying gold with nickel, an excellent and inexpensive whitener. The alloys produced had excellent characteristics, attractive colour, and good physical and mechanical properties. However, in recent years, greater attention has been given to the potentially toxic effect of nickel on the living tissue: allergic reactions having been documented (1). Because of this greater awareness of the potential risks of nickel, the European Community has a issued a European regulation, CE Directive 94/27, which aims to limit nickel content.

The aim of our present work is to document the preparation of nickel-free or of low-nickel 18 carat white gold alloys, which are both compatible with human users and have the physical, mechanical and commercial characteristics necessary for them to be competitive with other alloys in commerce today.

## Experimental Preparation

18 carat white gold alloy ingots were prepared by Leg.Or using materials with a purity of over 99.5% and a 99.99% Au content. The chemical compositions of ingots are summarized in Table 1.

These alloys were melted in graphite crucibles in an induction furnace, using boric-acid flakes as a flux. They were cast into graphite moulds and subsequently cold worked by rolling, (between a pair of 80 mm thick/150 mm wide rolls) to produce sheets about 1 mm thick, with a cross-section reduction of at least 65%. The OB-18, OB-19 and OB-20 alloys underwent a further process: annealing at 650° C, using an oxyacetylene torch for 5 seconds and cooling in alcohol, both done to simulate the working conditions typically used in goldsmith's workshops (2,3). A metal release (emissivity) measurement was then carried out in conformity with the European Directive prEN 1811:1996, using a Perkin-Elmer 819 Atomic Absorption spectrophotometer to determine the elements dissolved in an artificial sweat solution. The aim of this test was to measure the amount of nickel, expressed in $\mu g/cm^2$/week, released by a test sample immersed in a solution of artificial sweat for a week. The artificial sweat solution was an aqueous solution of sodium chloride, lactic acid, urea, ammonia and nitric acid. The test sample was suspended in the solution in a closed, Ni-free, glass container and kept perfectly still for 168 hours at 30° ±2°C. After this period, the sample was removed and washed with a little deionized water. This final test solution was used to determine the dissolved elements. Colour determination of the alloys was done with a VISSPECTRA 33 spectrum analyser using the CIELAB system. A microhardness test was executed using a LEITZ microdurometer with the Vickers penetrator set at a 100 g load.

**Table 1. Chemical composition of the alloys**

| | Ag %*wt* | Pd %*wt* | Cu %*wt* | Ni %*wt* | Zn %*wt* | Fe %*wt* | Mn %*wt* | Cr %*wt* |
|---|---|---|---|---|---|---|---|---|
| OB 1 | 10 | 5 | - | - | 1 | - | 9 | - |
| OB 5 | 14 | 5 | - | - | - | 6 | - | - |
| OB 11 | - | 2 | 10 | - | 5 | - | 8 | - |
| OB 18 | - | - | 14 | 5 | 3 | - | - | 2 |
| OB 19 | - | - | 16 | 3 | 3 | - | - | 2 |
| OB 20 | 14 | 4 | - | - | 2 | 5 | - | - |

**Table 2. Cielab colour co-ordinates of the alloys**

| Alloy | L | a | b | C |
|---|---|---|---|---|
| OB 1 | 83.8 | -1.03 | 0.30 | 1.08 |
| OB 5 | 83.1 | -0.56 | 2.03 | 2.13 |
| OB 11 | 84.0 | -0.36 | 0.73 | 0.82 |
| OB 18 | 83.6 | -0.83 | 1.53 | 1.74 |
| OB 19 | 84.8 | -0.36 | 1.73 | 1.77 |
| OB 20 | 77.9 | -0.70 | 2.73 | 2.91 |
| OB 18-R | 83.3 | -0.90 | 1.40 | 1.67 |
| OB 19-R | 81.1 | -0.36 | 1.76 | 1.80 |
| OB 20-R | 76.9 | -0.30 | 3.70 | 3.71 |
| *Au 99,99%* | *84.0* | *1.8* | *12.93* | *13.05* |
| *OB 325-F* | *87.4* | *-0.45* | *0.85* | *0.96* |
| *OB 304-R* | *86.5* | *-0.20* | *2.31* | *2.31* |

Note: L=brightness (from 0 for black to 100 for white); a= green (-a) to red (+a) axis; b=blue (-b) to yellow (+b) axis

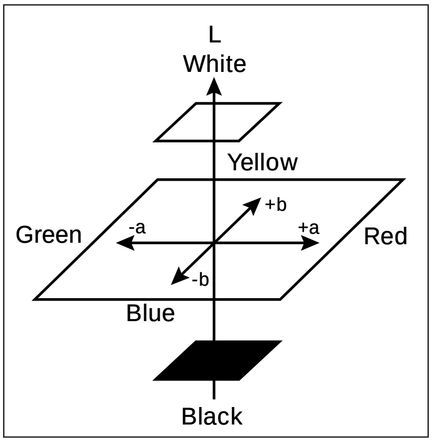

**Figure 1 -** CIELAB representation of colour co-ordinates

## Results

### *Colour*

Table 2 shows the CIELAB colour parameters (L, a, b & C values) of the alloys. The comparison is with 99.99% pure gold and two other commercial alloys, OB-325F and OB-304R. The OB-304R alloy shows a colour which is barely admissible without rhodium-plating. The CIELAB colour definition system (1) is expressed with help of three Cartesian co-ordinates, two of which form the chromatic plane, while the third measures the value of brightness. In the CIELAB representation, Figure 1, the white point is situated at the intersection of the a and b axis; the third co-ordinate L measures the brightness value of the sample, from 0 for black to 100 for white. When expressed in polar co-ordinates, the advantage of this system is to render the C distance (Chroma) a direct measurement of sample whitening. The value of C is calculated using the standard formula. Using the co-ordinate, C, it can be said that an alloy exhibits a better white colour when C tends to 0 (4).

It can be observed that all alloys exhibit a good white colour, except the OB-20 alloy, which is unusable, unless rhodium-plated to achieve an acceptable whiteness. Furthermore, it is important to note that annealing of alloy OB-20, even if for short periods, causes a notable yellowing which does not happen to OB-18 and OB-19 alloys.

### *Metal Release*

Table 3 shows the metal release results of the alloying elements, expressed in $\mu$g/cm$^2$\week and determined in conformity with the European Directive prEN 1811;1996. The OB-18 alloy shows a Ni emissivity well below the limit set by the CE Directive 94/27 (0.5 $\mu$g/cm$^2$\week). This value was slightly higher after a brief annealing. The reason for such an increase may be the coarsening and partial rearrangement of the grains, as can be seen in the micrographs, Figures 2 and 3, which produces a considerable reduction in corrosion resistance, as can also be seen in the increase of the emissivity values of the other elements. It is important to notice that nickel release in the OB-19 alloy is below the measurable limit and therefore denotes a negligible release of allergenic elements.

**Table 3. Metal release test results**

| Alloy | Ni | Zn | Mn | Fe | Ag | Cu | Cr |
|---|---|---|---|---|---|---|---|
| OB 1 | - | 0.43 | 0.00 | - | 0.00 | - | - |
| OB 5 | - | - | - | 0.00 | 0.22 | - | - |
| OB 11 | - | 0.36 | 0.12 | - | - | 0.83 | - |
| OB 18 | 0.30 | 0.56 | - | - | - | 0.46 | 0.00 |
| OB 19 | 0.00 | 1.00 | - | - | - | 1.50 | 0.00 |
| OB 20 | - | 1.57 | - | - | - | - | - |
| OB 18-R | 0.56 | 2.52 | - | - | - | 1.96 | 0.00 |
| OB 19-R | 0.00 | 3.83 | - | - | - | 4.26 | 0.00 |
| OB 20-R | - | 4.72 | - | - | - | - | - |
| *OB 325-F* | *0.52* | *0.53* | - | - | - | *0.69* | - |
| *OB 304-R* | *0.37* | *0.53* | - | - | - | *0.57* | - |

*Values expressed in* $\mu$*g/cm*$^{2\cdot}$ *week*

**Figure 2 -** OB-18 alloy before annealing (x 500)

**Figure 3 -** OB-18 R alloy after annealing

*Hardness*

Table 4 summarises the measured microhardness values of the alloys obtained. All the alloys have a hardness value slightly above 200 HV (the highest theoretical limit required for good working characteristics) (4). It should be kept in mind that all these alloys underwent a significant hardening during cold rolling and therefore present strong internal stress. In fact, after further heating the alloys at 650°C the microhardness values show a striking reduction in hardness, and for the OB-19R alloy are even as low as 200 HV. If the brevity of the annealing process (5 seconds) is considered, longer annealing periods should produce acceptable values.

**Table 4. Microhardness values of the alloys (Vickers hardness)**

| Alloy | Hardness HV |
|---|---|
| OB 1 | 297 |
| OB 5 | 254 |
| OB 11 | 345 |
| OB 18 | 388 |
| OB 18-R | 243 |
| OB 19 | 344 |
| OB 19-R | 195 |
| OB 20 | 297 |
| OB 20-R | 218 |
| *Au (99.99%)* | *76.6* |

*Melting Range*

The melting characteristics of the alloys displays a distinct subdivision into three groups, grouped according to the alloying elements present:

1) OB 1 and OB 11, with melting points (solidus) lower than 1100°C (the ideal limit for materials used in traditional casting systems), contain significant amounts of elements with low melting points and a percentage of palladium so low as to hardly affect the melting range.

2) OB 5 and OB 20, with a solidus of about 1100°C due to the concomitant presence of iron and palladium.

3) OB 18 and OB 19 with solidus temperatures higher than 1100°C due to the presence of chromium, which produces the rise in this value.

## Conclusions

It has been possible to produce white gold alloys completely or partially Ni-free. When present, the nickel percentage never rose to levels where allergenic problems would be produced when the alloy was in contact with the skin. Almost all the alloys had a good white colour and did not require rhodium plating. Palladium had to be used in the Ni-free alloys in order to obtain a satisfactory colour, even if this makes their production less economic. Promising results were obtained by using small amounts of nickel and chromium together. These materials, and particularly the OB-19 alloy, proved to be neutral and compatible with the nickel allergen limits set by the EC regulation. They also have the characteristics and properties required by jewellery manufacturers. However, one disadvantage remains to be solved: the very high melting point of these alloys requires further study, aimed at a reduction.

## References

1 ‘Nickel allergy: The European Directive and its consequences on gold coatings and white gold alloys’, P. Bagnoud, S. Nicoud, P. Ramoni, *Gold Technology*., 1996, **18**, 11

2 ‘Basic metallurgy for goldsmiths – VIII: Environmental effects...’, M.F. Grimwade, *Aurum*, 1981, **7**, 30

3 ‘18 carat white gold alloys’, P.C. Susz, *Aurum*, 1980, **4**, 11

4 ‘New white gold alloys’, I.B. MacCormack and J.E. Bowers, *Gold Bulletin*, 1981, **14**, 19