

# Strong 24 carat golds: The metallurgy of microalloying

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## Introduction

As we know, pure metals tend to be soft and ductile and gold is the ultimate example, being very soft and the most malleable (ductile) of all pure metals (1). In the modern production of gold jewellery, this softness is of little advantage in jewellery manufacture (2) and a disadvantage in service when items are liable to distort, fracture and scratch and wear heavily during use. It is one of the main reasons why much gold jewellery is made from carat golds where alloying with copper, silver and other metals confers hardening and other property improvements as well as colour variation.

Today, gold jewellery is purchased mainly for adornment in the Western cultures whereas in the Eastern cultures, it is bought primarily as a store of value, a readily tradeable investment in times of economic and political instability. This difference in attitude is reflected in the caratages of gold used in jewellery with high carat golds preferred in the East and low-medium carat golds preferred in the West, as shown in Table 1. As you will note, 24 carat 'Chuk Kam' jewellery is dominant in the Chinese countries of the Orient. Chuk Kam - meaning pure gold - is defined in the main Oriental countries as a minimum of 99.0% gold. In others, it is defined as 99.5% or higher (See Table 1 in Reference 3). The region consumes over 400 tonnes of gold per annum, about 15% of total world jewellery fabrication, and this figure is growing as the Chinese economy develops.

## 24 carat gold jewellery

Increasingly, there is a trend to buy 24 carat gold jewellery for adornment as well as investment, particularly by younger people. It is significant that in many markets around the world, major branded collections in 24 carat gold have been launched.

However, normal 24 carat gold, whether 99.0%, 99.5% or 99.9% purity (with silver as the major impurity), is too soft for jewellery purposes with a very low hardness of about HV 20 - 30 in the annealed, soft condition rising to only HV 50-80 in the cold worked condition. In contrast, a standard yellow 22 carat gold-copper-silver alloy has an annealed hardness of about HV 52, rising to about HV 140 in the work hardened condition, and an 18 ct standard yellow gold-silver-copper alloy has an annealed hardness of HV 150, rising to HV 225 in the work hardened condition and even higher in the age-hardened condition (4). The importance of alloying in enhancing properties is evident. Clearly, the development of a 24 carat gold with enhanced mechanical properties, particularly strength and hardness, would be welcomed by the consumer.

Recognising this, World Gold Council sponsored the development of an alloy of 99.0% purity back in the mid 1980s with considerably enhanced properties. Alloyed with 1% titanium, a hardenable alloy known as '990 Gold' was successfully developed. Its development is detailed in *Gold Bulletin* (5) and *Gold Technology* (6). Table 2 shows its main properties.

As can be seen, it has a much higher hardness than pure gold and 22 ct yellow gold in the soft, annealed condition and is similar to 22 ct yellow in the work hardened condition, although still not as hard as 18 carat yellow. However, in the age-hardened condition, it is very similar to the hardness values obtained in the 18 ct material and is much superior to conventional 22 and 24 carat golds which are not age hardenable. Clearly,

**Table 1. Typical Caratages of Gold Jewellery**

Region	Typical Caratage (fineness)
Oriental East (China, Hong Kong, Taiwan)	24 carat 'Chuk Kam' (99.0% min)
India	22 carat (91.6%)
Arabic countries	21 carat (87.5%)
Europe - Southern *	18 carat (75.0%)
Europe - Northern, USA, etc**	8-18 carat (33.3 - 75.0%)

\* Portugal - 19.2 carat (80.0%)

\*\* For example, Germany - 8,14 and 18 carat; UK - 9 ct; USA - 10,14 and 18 carat

**Table 2. Properties of '990 Gold'**

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

\* Range depends on whether aged in annealed, cold worked or aged and cold worked condition

the development of '990' gold-titanium alloy represented a significant breakthrough in enhancing the properties of gold, hallmarkable in many countries as 24 carat (990 fineness).

Unfortunately, the production of the '990' alloy requires sophisticated vacuum melting and processing procedures, and scrap cannot simply be remelted and recycled. As a consequence, '990' gold has only really seen application in the watch industry, and is little used in the jewellery industry today, despite its potential.

### Strong 24 carat golds

In recent years, a number of improved strength 24 carat golds have been developed (3, 7-11, 20), some commercially available as semifinished products, and jewellery produced in these is in the market place, particularly in Japan, Figure 1. These are listed, with their mechanical properties in Table 3. They have virtually the same melting point, colour and density as normal pure gold.

It is evident from Table 3 that, whilst annealed hardness is usefully higher than that for normal pure gold, cold working results in significant hardness increases and that some materials may be further hardened by low temperature ageing heat treatment. Perhaps not surprisingly, the highest

hardnesses are achieved in the lower purity golds of 99.5 – 99.7% fineness. Most can be cast but the best hardnesses are achieved in the wrought condition, often coupled with ageing treatments. These stronger alloys do influence manufacturing processes. For example, machine-made chain can be made from them with less difficulty than with normal pure gold. Of course, they also confer jewellery with better wear and scratch resistance and greater strength, so resisting distortion and damage.

When compared to standard yellow carat golds, we can see that these improved 24 ct golds approach the hardness of 22 ct gold in both annealed and cold worked conditions



Figure 1 - Jewellery in High Strength Pure Gold (9)

Table 3. Improved Strength 24 ct Golds

Material	Manufacturer	Purity	Annealed Hardness, HV	Cold Worked Hardness, HV	Strength, MPa	Ductility, %	Comments
High Strength Pure Gold	Mitsubishi, 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
Pure Gold	Three O Co, Japan	99.7%*	63	106 Aged: 145 - 176	–	–	Castable, Hardenable, Chain
Uno-A-Erre 24 ct Gold	Uno-A-Erre, Italy	(i) 99.6% (ii) 99.8%	33 62	87 118	–	–	Both used in CW condition
DiAurum 24	Titan, UK	99.7%	60 (as cast)	95	–	–	Castable
Pure Gold	–	99.9	30	50	190 - 380	Anneal: 40 CW: 1	
22 ct Yellow (5.5 Ag - 2.8 Cu)	–	91.7%	52	100 - 138	220 - 440	Anneal: 27 CW: 3	Castable
18 ct Yellow (12.5 Ag - 12.5 Cu)	–	75.0%	150	190 - 225 Aged: 230	520 - 900	Anneal: 40 CW: 3 Aged: 15	Castable, Age Hardenable

CW - cold worked \* based on patent. Reference (20) describes Pure Gold as 99.85% gold

but are some way off the hardness values for 18 ct gold, despite some claims by manufacturers.

It is surprising that such improvements in strength and hardness can be achieved in gold with alloying additions of only 0.5% wt. or even down to 0.1%. Such small alloying additions can be described as *microalloying*. How are such property improvements possible in microalloyed gold? It is instructive, therefore, to look at hardening mechanisms in gold alloys. The reader may find the next sections easier to understand if they have read Mark Grimwade's articles on phase diagrams in *Gold Technology*, nos 29 and 30 published in 2000.

## Basic mechanisms of hardening

### 1. Hardening by grain size control

Firstly, we should note that all metals and alloys are crystalline. All the metal atoms sit in a regular crystal lattice and a bulk alloy consists of many crystals – or grains, as metallurgists call them – each oriented in different directions. In pure gold, all atoms are gold atoms of exactly the same size and so the crystal lattice is regular, with flat, smooth crystal planes. The smaller the size of the crystals or grains in the alloy, the higher is the alloy strength. This is strengthening by grain size control – the Hall-Petch effect – where the flow strength is inversely proportional to the square root of the grain diameter. For gold jewellery, this is not a significant hardening mechanism

### 2. Solid solution hardening

In carat gold alloys, some of the gold atoms are substituted in the crystal lattice at random by atoms of the alloying metals, such as silver, copper and zinc. As atoms of different metals are of a different size, their inclusion in the lattice leads to a distortion of the

lattice and the crystal planes become less smooth. Since deformation of the crystal takes place by the sliding of crystal planes over each other (through lattice defects known as dislocations moving through the lattice), any distortion of the lattice by atoms of other metals will increase the force necessary to slip the planes over each other. This is known as *substitutional solid solution strengthening*. Silver atoms are a little different in size to gold atoms (actually a little larger) whereas copper atoms are much smaller (by about 12%) and cause greater distortion of the lattice. Hence copper is more effective than silver in strengthening gold, as seen in Figure 2. In general, the more alloying atoms, the more the strengthening effect. That is why 22 carat (91.6% gold) alloys are stronger than pure gold and 21, 18, 14 and lower carat golds even stronger. At 24 carat (990 fineness), gold cannot be effectively hardened by normal alloying.

### 3. Work hardening

Of course, as we all know, deforming or cold working a pure metal or alloy hardens it. This is known as *work hardening*. This technique of hardening has a limit as ductility reduces and eventually the material will fracture, if it is overworked. But some cold-working is a very effective way of improving the strength of pure gold and carat gold alloys. The only drawback is that the object must not be subsequently heated, for example, during soldering or by annealing, as this will cause any work hardening to be lost. A real problem in actual jewellery manufacture.

### 4. Hardening by second phases

For many real alloys, it is not possible for atoms of alloying metals to substitute for the parent gold atoms beyond a certain concentration. Silver can completely substitute for gold atoms at all concentrations, but in silver-copper alloys, for example, copper can only substitute in silver up to a limit which reaches a maximum of 8.8 wt% at 779°C. Beyond that limit, an additional copper-rich phase is formed to yield an alloy consisting of two phases – a silver-rich phase and a copper-rich phase with different sized crystal lattices. A two-phase structure is normally stronger than a single phase

structure. The degree of strengthening depends on the relative sizes of the different phases and their distribution. Such two phase structures extend into the gold-silver-copper alloys up to about 18 ct in certain composition ranges.

In the case of gold - copper alloys, copper can substitute for gold in the solid state at all concentrations only above a temperature of about 410°C. Below this temperature, one of two intermetallic compounds form at certain specific compositions and, depending on their size and distribution, can effect considerable strengthening to high copper-containing carat golds up to about 18 carats fineness. These intermetallic phases are ordered structures in which the gold and copper atoms sit on specific sites in the crystal lattice (rather than at random, as in solid solution hardening). In this case, they form alternative layers of gold and copper atoms. This is a more difficult structure to deform and hence is harder.

The presence of hard, small particles of a second phase at grain boundaries and within the grains (or crystals) impedes the passage of dislocations (the crystal defects which enable deformation of the crystal under stress) through the crystal lattice and a higher force or stress is needed to deform the metal or alloy. This mode of strengthening is called *dispersion hardening* and is particularly effective at higher temperatures.

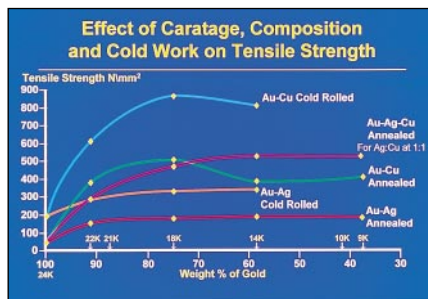


Figure 2 - Effect of alloying and cold work on the properties of gold

These fine dispersions of hard particles may be oxides, carbides (in the case of steel) or precipitates of second phases such as the ordered gold-copper intermetallic compounds (hence it is also known as *precipitation hardening*). The formation of such fine dispersions of precipitates of second phase can be controlled by low temperature heat treatment - known as *age hardening* - to confer considerable strengthening. Copper-containing gold-silver-copper alloys between 8 and 18 carats can be substantially hardened by such treatments as mentioned earlier.

The smaller the particles or precipitates and the more of them present, the greater the degree of strengthening. Thus, considerable strengthening can be obtained by relatively small volume fractions of particles provided they are very fine in size and well dispersed. This fact gives us a clue to the design of microalloyed

24 ct golds, since it is unlikely that significant strengthening of pure gold can be achieved from just control of grain size or solid solution hardening.

The use of small fractions of fine oxide particles to provide dispersion hardening of gold is reported in the literature. Poniatowski and Clasing reported (12) that a dispersion of 0.42%wt (1.85% vol) titanium dioxide particles, 0.5µm diameter, gave an annealed hardness of HB 55, compared to HB 20 for pure gold, which rose to HB 80 after coldworking 80% reduction. Tensile strength was about 190 N/mm<sup>2</sup> compared to about 75 N/mm<sup>2</sup> for pure gold. Hill (13) studied mixtures of gold powder and oxides of thorium, aluminium, yttrium, cerium and titanium to produce dispersions of oxides up to 1.00% by volume (0.18 - 0.38% wt). Annealed hardnesses ranged from HV 51 - 65, which increased to HV 67-82 after 82% cold work. The tensile strengths

ranged from 153 - 207 N/mm<sup>2</sup> compared to 112 N/mm<sup>2</sup> for pure gold. These studies demonstrate that dispersion hardening can enable substantial hardening of gold at low concentrations. However, such alloys are not commercially available and are not the basis of the new strong 24 ct golds.

### 5. The density effect on alloying

To complete this section, mention must be made of the difference between atom weight and size or volume. The higher atomic numbered metals are larger and also heavier. Gold is a heavy metal with a density of 19.3 g/cm<sup>3</sup>, whereas silver has a density of 10.5 g/cm<sup>3</sup> and copper a density of 8.93 g/cm<sup>3</sup>. Thus, in describing alloys we must differentiate compositions given in terms of weight percent - the relative weights of alloying metals present - and compositions given in terms of atomic percent, i.e. how many atoms

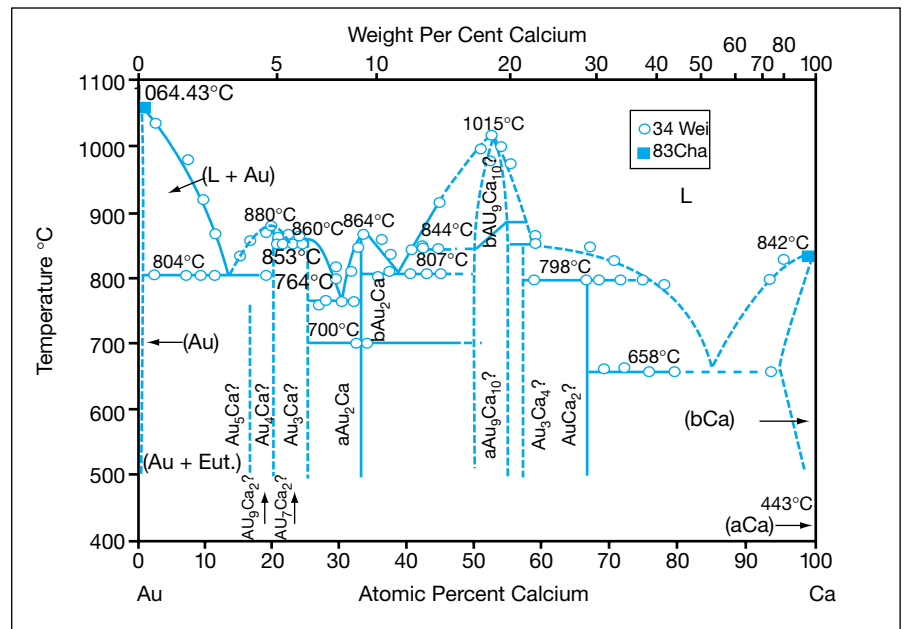


Figure 3 - The gold-calcium phase diagram

Table 4. Possible Light Metals for Alloying into Gold

Metal	Atomic Number	Atomic Weight	Density, g/cm <sup>3</sup>
Lithium	3	6.9	0.53
Potassium	19	39.1	0.86
Sodium	11	23.0	0.97
Calcium	20	40.1	1.53
Magnesium	12	24.3	1.74
Beryllium	4	9.0	1.85

**Table 5. Features of Gold – Rare Earth Phase Diagrams**

Rare Earth	Solid Solubility in gold	Intermetallic compound	Eutectic, at% gold (temperature, °C)	Comment
Lanthanum	v.low	Au <sub>6</sub> La	91 (808)	OK
Cerium	v.low	Au <sub>6</sub> Ce	90.5 (808)	OK
Praeodymium	v.low	Au <sub>6</sub> Pr	88 (808)	OK
Neodymium	v.low	Au <sub>6</sub> Nd	90.5 (796)	OK
Samarium	v.low	Au <sub>6</sub> Sm	88.5 (770)	OK
Gadolinium	low (0.7 at%*)	Au <sub>6</sub> Gd	90.5 (804)	Age-hardenable?
Dysprosium	2.1 at%*	Au <sub>6</sub> Dy	90.5 (808)	Age-hardenable?
Erbium	5.7 at%*	Au <sub>4</sub> Eb	88.6 (734)	Age-hardenable?
Terbium	1.5 at%*	Au <sub>6</sub> Tb	90.3 (798)	Age-hardenable?
Lutetium	7.7 at%*	Au <sub>4</sub> Lu	84.8 (890)	Age-hardenable?

\* Solubility at the eutectic temperature; this reduces as the temperature falls.

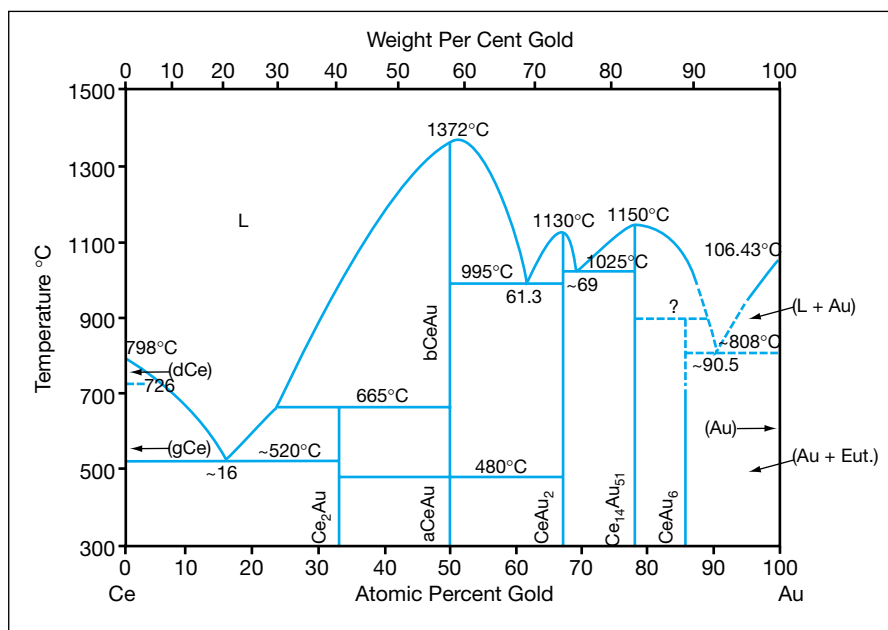
there are of each metal in the alloy. This point is illustrated by gold-copper alloys. An alloy of 50% gold atoms and 50% copper atoms, i.e. 1 gold atom to each copper atom, has a weight % composition of about 75% gold and 25% copper, reflecting the difference in weight of the gold and copper atoms!

**Microalloying of gold**  
*The Theoretical Basis for Microalloying*

In the development of strong 24 carat golds, we are looking at total alloying additions of 0.5 wt% or less, even down to only 0.1 wt% in some instances, to effect a dramatic strengthening of the gold crystal lattice. Such small additions are approaching those typically used to control grain size (the so-called ‘grain refiners’). As gold is a low stacking fault metal (stacking faults are 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 only way such small additions might contribute to significant solid solution hardening is if the alloying metal is very light, i.e. it has a low density and there is a large difference in atom size to gold. If we examine the Periodic Table, the light metals that might be possible microalloying additions are, in order of density: lithium, potassium, sodium, calcium, magnesium and beryllium, Table 4.

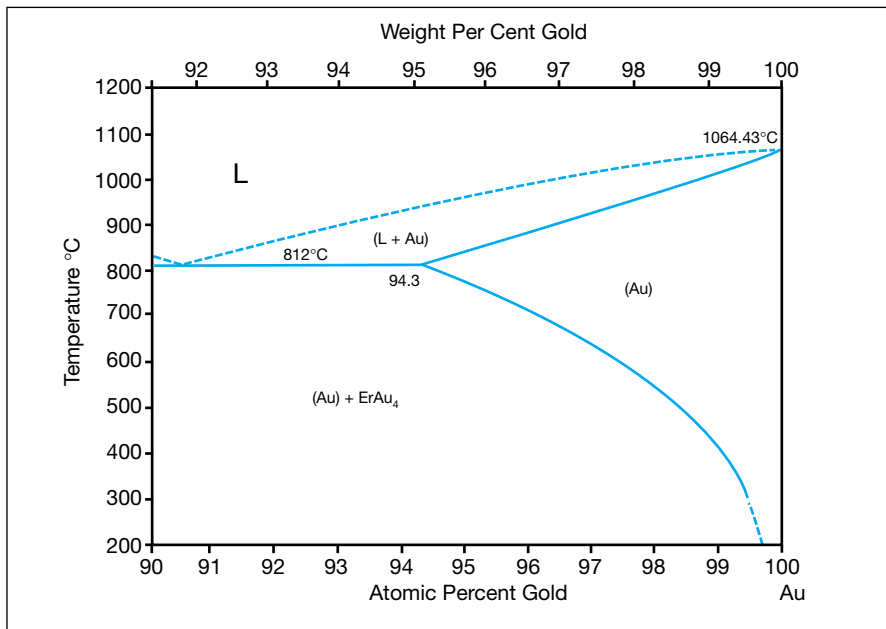
Taking the lightest metal in Table 4,



**Figure 4 - The gold-cerium phase diagram**

a gold - 0.5 wt % lithium alloy, for example is 12.55 at% lithium which is within the solid solubility range. This is about 1 atom of lithium to every 7 atoms of gold. In comparison, a gold - 12.55 at% copper alloy is only 4.4 wt% copper which would increase hardness in the annealed condition to about HV 40 and to about HV 80 in the cold worked condition. So maybe a gold-lithium alloy could provide the necessary property improvement by solid solution hardening, but it is doubtful.

If we look at another light metal, calcium, a gold-0.5 wt.% calcium alloy is only 2.41 at% calcium which is quite



**Figure 5** - The limit of solid solubility at the gold-rich end of the gold-erbium phase diagram

small – only 1 atom in 40 – and, therefore, would not be expected to provide much solid solution strengthening. However, reference to the phase diagram, Figure 3, shows that there is virtually no solid solution of calcium in gold and that there is a eutectic comprising two phases of which one is gold and the other an intermetallic compound of high gold content, probably  $Au_4Ca$  or possibly  $Au_5Ca$ .

If this latter phase is finely dispersed in the microstructure, then we have the basis of a possible alloy system that could provide improved properties through dispersion hardening. In the as-cast condition, we would anticipate a structure of primary dendrites of gold edged with regions of the eutectic mixture of the 2 phases. However, on cold working and annealing, this structure would be broken down and refined to yield gold grains pinned by fine particles of the second phase of intermetallic  $Au_4Ca$  (or  $Au_5Ca$ ).

We find similar features to the gold-calcium system in the phase diagram for the gold – potassium system, but less strongly (i.e. lower gold-containing intermetallic compounds) in the gold –

beryllium, gold – magnesium and gold – sodium phase diagrams, suggesting that they are less favourable for a microalloying approach.

Another alloying approach would be to add the rare earth metals, such as cerium, lanthanum and dysprosium, as these also tend to have limited solid solubility in gold and to form eutectics and intermetallic compounds of high gold content. Table 5 lists some relevant features of their phase diagrams with gold. Some rare earths have been omitted for brevity.

From this table, it can be seen that the light rare earths are potentially suitable. Figure 4 shows the phase diagram for gold-cerium. The similarity to the gold-calcium system at the gold-rich end is evident. Also, as the ‘heavy’ rare earths have a solubility at the eutectic temperature in excess of 0.5% but a very low solubility as the temperature falls, it is possible that they may be amenable to age-hardening treatments, with the precipitation of fine particles of the intermetallic on annealing quenched material at low temperatures. This is illustrated in Figure 5, which shows the region of solid solubility for gold-erbium alloys.

#### **Previous work on gold - rare earth alloys**

In the development of the 990 gold-titanium alloy, Gafner (5) describes work on other candidate alloy systems, which included the heavy rare earths. The basis for selection was the possibility of second phase precipitation as an alloy containing a 1 wt% alloying addition in solution was cooled from 800°C to 400°C. From this,

**Table 6. Candidate Alloy Systems and Probable Hardening Effects, [from Gafner, reference (5)]**

System	Solubility at 800°C	Solubility at 400°C	Fraction* wt%	Ratio, atomic weight	Fraction* at%	Fraction hardening 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	0.0	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.

**Table 7. Hardnesses of Gold – Rare Earth Alloys (from reference 14)**

Alloy Composition, wt%	Hardness, As cast HV	Hardness, Annealed HV	Hardness, 95% CW HV*	Hardness, Aged 300°C HV*
Au - 0.3 Gd	44	30	130	63
Au - 0.5 Gd	34	48	115	85
Au - 0.5 Tb	44	30	110	67
Au - 0.5 Dy	70	29	120	75
Au - 0.3 Y	35	24	110	45
Au - 0.4 Y	32	34	120	–
Au - 0.5 Y	61	38	145	174

\*Approximate values taken from graphs. CW-cold worked.

a table of probable hardening effectiveness was constructed, Table 6.

The fraction of hardening phase in the last column was taken as an indication of hardening effectiveness. The reason for developing the 990 gold-titanium alloy is obvious from this table. The promise of the rare earths and zirconium should also be noted.

However, in this work, a 1 wt% alloying addition was being evaluated. If we consider only a 0.5 wt% addition of rare earth, then from the solubility data at 400°C in Table 5, we cannot expect much hardening phase to precipitate on annealing material which is in solution at 400°C.

Fortunately, some tests have been carried out (14) on some gold-rare earth alloys, at alloying levels of 1 wt% and lower. Cast alloys were annealed at 800°C for 1 hour. They were also cold rolled up to 95% deformation and subjected to age hardening treatments at a range of temperatures. Table 7 shows the hardness values attained for gold alloys containing 0.5% or less addition.

From this work, it can be seen that the annealed hardness is little different from normal pure gold, although cold worked material is much harder and in the range of the strong 24 carat materials (Table 3). Age hardening heat treatments are not very effective at these low concentrations with the exception of the 0.5% gold-yttrium alloy (and yttrium is not strictly a rare earth metal). This supports the view expressed earlier in that consideration of the solubility data, Table 5, of the heavy rare earths suggests little age hardening is possible at these low alloying levels. Whether alloys of gold with the light rare earths show good properties is not known from this

work. It is difficult to comment on the results for gold-yttrium alloys as there is no published gold-yttrium phase diagram (15), but recent work by Ning (16) indicates that it is similar to the heavy rare earths with some solid solubility (about 2 at%) of yttrium in gold.

#### **Compositions of actual Strong 24 ct golds**

The theoretical possibilities for microalloying gold have been discussed. But what do we know about the real materials. Unfortunately, few patents or papers have been published on the compositions of the materials that have been developed to date (Table 3). However, there is some information, mostly patents, which are now discussed.

#### **1 High Strength Pure Gold - Mitsubishi Materials Corporation**

Mitsubishi have several patents in this area. In their main patent (17), they claim gold alloys of 99% purity or higher containing 200 – 2000 ppm of one or more of the following elements: calcium, beryllium, germanium and boron. From other sources (18, 19), it is clear that calcium is the principal hardening metal in High Strength Pure Gold. Examination of the phase diagrams for gold-beryllium, gold-germanium and gold-boron shows similarities with gold-calcium, so similar effects on microstructure and properties are anticipated. The patent also includes further additions of 10 –1000 ppm of one or more of many metals including magnesium, aluminium and cobalt and/or 10-1000ppm of rare earth metals and yttrium. The hardness values for over 50 alloys quoted in their patent lie

typically in the range HV 100 - 140 which is consistent with the claimed properties for High Strength Pure Gold.

In a further patent (19), an alloy of 99% gold or higher is claimed containing 500-2000ppm calcium and 1-50ppm carbon. The role of carbon is not clear, but may harden interstitially or preferentially segregate with some calcium to grain boundaries.

#### **2 PureGold - Three O Company**

In their patent (9), an age hardenable alloy of 99.7% gold with a hardness comparable to an 18 carat gold is claimed containing 50 ppm or more gadolinium and optionally a third metal – calcium, aluminium or silicon – the total being in the range 100-3000 ppm. For an alloy containing gadolinium and calcium, a maximum hardness after a combination of working and ageing of HV 176 is described which is consistent with the published hardness of PureGold, Table 3. The optimum ageing temperature is 250°C. The properties of PureGold are discussed by Bernadin in an earlier issue of *Gold Technology* (20) where it is claimed that the commercial alloy is 99.85% gold.

### 3 Other Golds

From private discussions, it is clear that calcium is used in combination with other alloying metals in some of the other golds listed in Table 3. The basis for the Mintek Hard 24 ct Gold is unknown at the time of writing. In a patent from Tanaka KK, Japan (21), an alloy for precision casting is claimed containing small amounts of hafnium and rare earth metals.

In some reports (7, 8), the cold working of the surface during finishing plays an important role in hardening the surface.

### 4 Other Literature

Doped pure gold wires are used extensively in the electronics industry for bonding. In a recent paper (22), Lichtenberger and colleagues doped high purity gold (5-9's purity) with 3-30 ppm of aluminium, calcium, copper, silver and/or platinum. They showed that most dopants strengthened the wire during extrusion (beryllium had the largest effect) but only calcium and beryllium had significant strengthening effects after annealing. This is explained on the basis atom size difference in the gold lattice: Calcium atoms are about 30% larger and beryllium atoms are about 30% smaller than gold. There will be a tendency for calcium atoms to sit on grain boundaries and pin them at these low concentrations.

Various patents for improved strength gold bonding wires cite, respectively, additions of bismuth, rare earths, calcium with beryllium, europium with niobium, germanium, barium, yttrium with rare earths, and calcium with lead. The use of calcium, beryllium and/or the rare earths seems to be a popular choice in this application.

### Making jewellery in microalloyed Strong 24 ct golds

The papers published in recent issues of *Gold Technology* (7, 20) discuss the practical attributes of microalloyed golds for jewellery making. For example, Bernadin (20) has shown that PureGold (as with some of the other golds) can be investment cast as well as worked by normal techniques. Chain making by machine is certainly possible and the high strength of the alloy enables lightweight strong chains to be made with good wear properties. The good mechanical properties of such materials enable springs, screws, catches and findings to be made satisfactorily, as he illustrates in his article.

#### 1. Melting, casting and fabrication

All of these new high strength alloys contain alloying elements that are highly reactive with oxygen and, therefore, melting and casting really needs to be in an inert atmosphere or under vacuum. This obviously places restrictions on the production of the alloys; they cannot be made by melting the constituents together in air. So small factories and workshops would need to buy in semifinished product from the alloy suppliers. However, subsequent fabrication will be straightforward. Rolling, wire drawing, tube fabrication, chain making, etc are all possible in the small workshop. However, an understanding of the materials is also essential as some of the alloys are heat treatable and the treatments need to be carefully controlled. Additionally, annealing may destroy some of the benefits although it is unlikely that conventional annealing treatments will be necessary with these alloys as they should be able to withstand a high degree of cold work.

For those alloys that are heat treatable, the ideal processing steps would comprise an initial solution treatment (temperature dependent on the particular alloy), water quench, cold work to finished product, precipitation treat (age harden) at low temperature to develop final hardness. For castings, the procedure would comprise solution treatment, quenching and precipitation hardening.

As noted earlier, Table 3, many of these strong golds can be investment cast satisfactorily. Conventional

gypsum-bonded investments are not recommended. Either coating the mould surface with a refractory (7) or use of phosphate-bonded investment (20) is recommended. Melting and casting under a protective atmosphere in a static machine is preferred.

#### 2. Soldering and joining

There are two main issues that have to be addressed when considering soldering of 24 carat golds. Firstly, it is obviously not possible to find a solder of equivalent caratage to the parent metal as all these 24 carat gold alloys, with up to 0.5% of alloying elements, possess melting points within a few degrees or so of the melting point of pure gold (1064°C). This has significant implications for those countries with strict Hallmarking laws and, indeed, for simple marking of jewellery with a caratage mark. In the UK, which perhaps has the strictest Hallmarking laws of anyone, the two 24 carat golds legally allowable (990 and 999 finenesses) can be soldered with 22 carat gold solders provided excessive use is not made of the solder. Thus there must be no trace of using solders for filling purposes. In the USA, where Hallmarking does not exist, the law will allow manufacturers to mark their jewellery 24 carat if it is at least 99.7% purity and without solder joints. For fabricated jewellery, which contains soldered joints, the overall purity must be at least 99.3% for the item to be marked 24 carat. As an example, for a 10g item of jewellery to be marked 24 carat, 0.5g of 22 carat gold solder could be incorporated into 9.5g of 99.7% pure gold. The situation, therefore, varies from country to country and may, in fact, not even have been considered in some.

The second issue to consider in soldering 24 carat golds is the possible effect of the soldering operation on the alloy properties. Using conventional 22 carat gold solders which melt at temperatures of 800 - 950°C is going to cause a loss of work hardening in the immediate vicinity of the joint (throughout the whole piece if furnace soldering) and also a similar loss of the precipitation hardening due to overageing. Possible ways of overcoming this problem might be to use laser or microplasma torch welding or capacitor discharge welding where the applied heat is very localised and of short duration.

Alternatively, if the soldering operation could be combined with a solution heat treatment and followed by quenching and precipitation hardening, this could work for some alloys. Finally, there are 22 ct solders (23) which have very significantly lower melting points than the usual gold solders. One such alloy is available in paste form and has a melting point of 361°C and with such alloys it is possible to carry out soldering with little or no loss in strength (7).

### **3. Finishing**

Polishing of jewellery in these strong golds should be easier than normal pure gold as they are harder and a good high polish should be attained. Bernadin notes (20) that castings require similar polishing procedures to platinum, as PureGold does not flow in the same way as 14 ct gold. Use of magnetic polishing to harden the surface of castings during finishing is recommended for High Strength Pure Gold (7)

### **4. Recycling of scrap**

An important practical point is that, as far as published information tells us, these materials cannot be simply remelted and recycled without loss of strength (7), as the hardening microalloying additions lose their effect on remelting. Recycling of these alloys without loss of the strength is possible only as long as contact of molten metal with oxygen is avoided. In other words, melting must always be in an inert atmosphere or in vacuum and this may be a significant restriction on their use. It is also important to be aware that mixing with conventional alloys and remelting or recycling is likely to result in oxidation of the microalloying elements and the possible formation of oxide inclusions, with the loss of any potential strengthening.

However, the overall gold content is recovered on remelting, even if the microalloying metals are oxidised, leaving pure gold which can be used for conventional alloying to make normal carat gold alloys (7).

### **Application of microalloying to 21 and 22 carat golds**

The microalloying approach discussed for improving the strength

of 24 carat gold should also be applicable to high carat golds such as 21 or 22 carats, where age-hardening by conventional alloying with copper is not viable. The copper and silver additions to high carat golds may influence the phase diagram characteristics described for the binary gold alloys, but the principles are still valid. However, there may also be scope for strengthening high carat golds by conventional alloying techniques. There is some evidence that cobalt additions are effective in conventional 22 carat gold. The recent announcement of an age hardenable Hard 22 ct Gold by Mintek (24) with hardnesses of up to HV 233 shows that it is possible, but as yet there is no indication of whether it is achieved by microalloying or by conventional alloying. This alloy can be investment cast in air under a flux cover.

### **Conclusions**

A number of strong 24 carat golds of at least 99.5% purity have been developed in recent years, using a microalloying approach. The theoretical basis for strengthening by such small amounts of alloying elements has been reviewed and some possible candidate alloying additions discussed on the basis of strengthening by precipitation hardening or a dispersed phase arising from a eutectic reaction during solidification. Subsequent refinement of the dispersed phase by cold working plays an important role. In general, the alloying addition should have a low solid solubility in gold at ambient temperatures and form an intermetallic compound of high gold content.

This alloying approach has been compared to known published information on the new 24 ct golds. The key alloying additions have been shown to include calcium, beryllium and the rare earth metals as suggested by the theoretical analysis.

The practical aspects of making jewellery in these new golds has also been discussed

The adoption of the microalloying approach to the high carat golds such as 21 and 22 carats is considered possible.

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