THE METALLURGY OF THE COLOURED CARAT GOLD ALLOYS

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Despite the fact that this topic
was last reviewed in this Bulletin in 1978,
there was until 1989 little of significance
reported in the scientific and technical literature
to justify an updating of the position.
The reporting in that year [1] of the 990 gold-titanium alloy
as suitable for fabrication of gold jewellery of
this fineness (23.76 carat) has changed this position.
This further review therefore consists essentially of
two parts:

In the first,
the conventional coloured carat gold alloys based on 120
Au-Ag-Cu and Au-Ag-Cu-Zn systems are discussed. The
treatment follows that of McDonald and Sistare [2]
and is largely a resumé of their excellent review
which has features that well merit being brought to
the attention of readers again.

In the second,
the new 990 Au-Ti alloy is discussed
with special reference to its potential for use by
goldsmiths and manufacturers.

The Coloured Gold Alloys Based on the Au-Ag-Cu and Au-Ag-Cu-Zn Systems

Alloys Based on the Au-Ag-Cu System

The metallurgy of the coloured gold alloys was reviewed by A.S. McDonald and G.H. Sistare of Handy and Harman (Fairfield, Conn., U.S.A.) in 1978 [2]. They considered first the alloys of the Au-Ag-Cu system, from which all the carat gold alloys in this class inherit certain fundamental metallurgical characteristics. They detailed these and demonstrated (see below) how the introduction of zinc in the amounts (up to 15 %) in which it may be present in Au-Ag-Cu-Zn carat gold alloys modifies them. The very important contribution of these authors was their analysis of the properties of Au-Ag-Cu alloys in terms of three quasi-binary vertical sections (**Figure** 1) of the ternary diagram at constant gold contents corresponding to caratages of 18, 14 and 10 respectively. (The section for a caratage of 9 may be taken to be very similar to that for the caratage of 10).

Instead, however, of plotting the silver concentrations on the abscissae, to designate alloy composition, they used a parameter Ag', which was defined as:

$$Ag' = \frac{Ag\ (wt.\%)}{Ag\ (wt.\%) + Cu\ (wt.\%)} \times 100\ \%$$
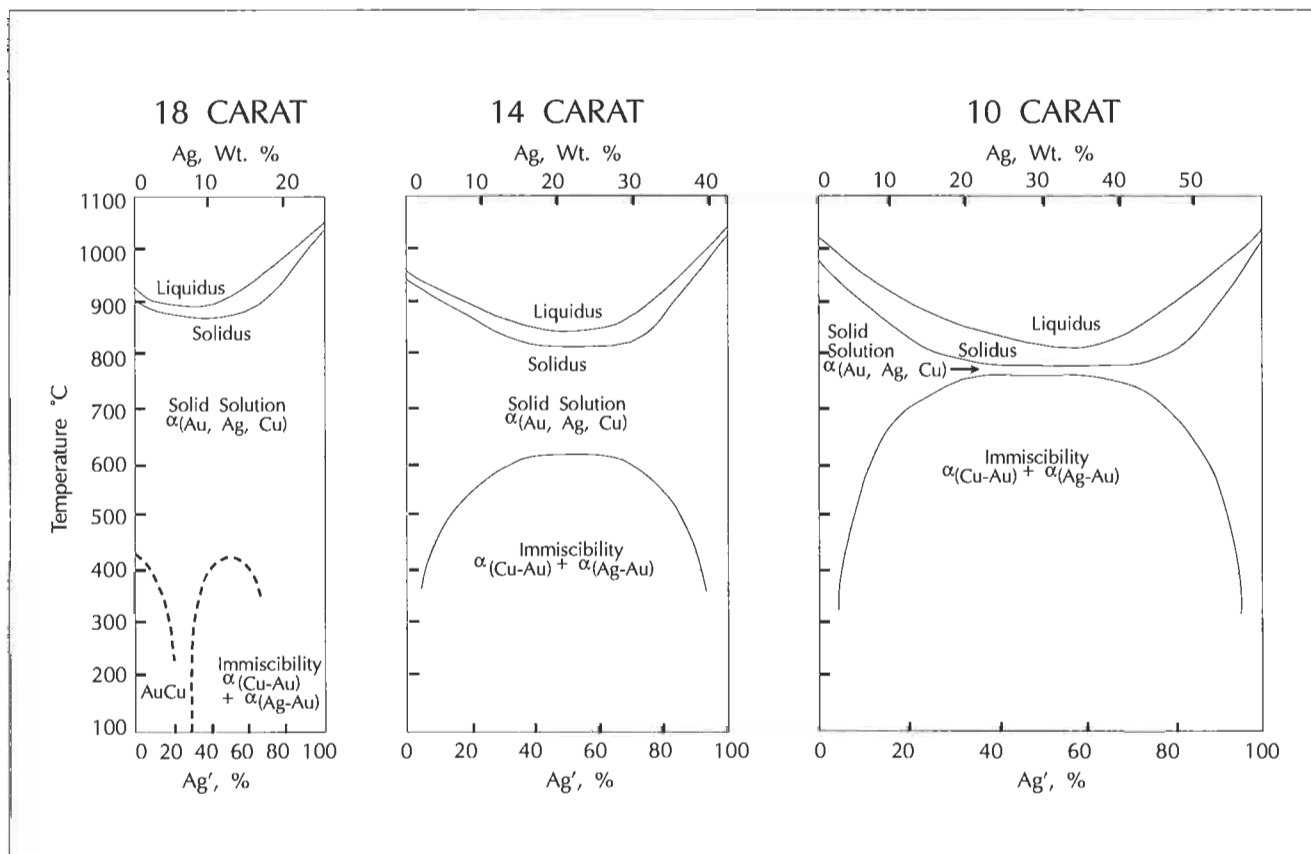

Figure 1

Schematic quasi-binary sections at constant caratage of the gold-silver-copper ternary phase diagram. The parameter Ag' is defined in the text.
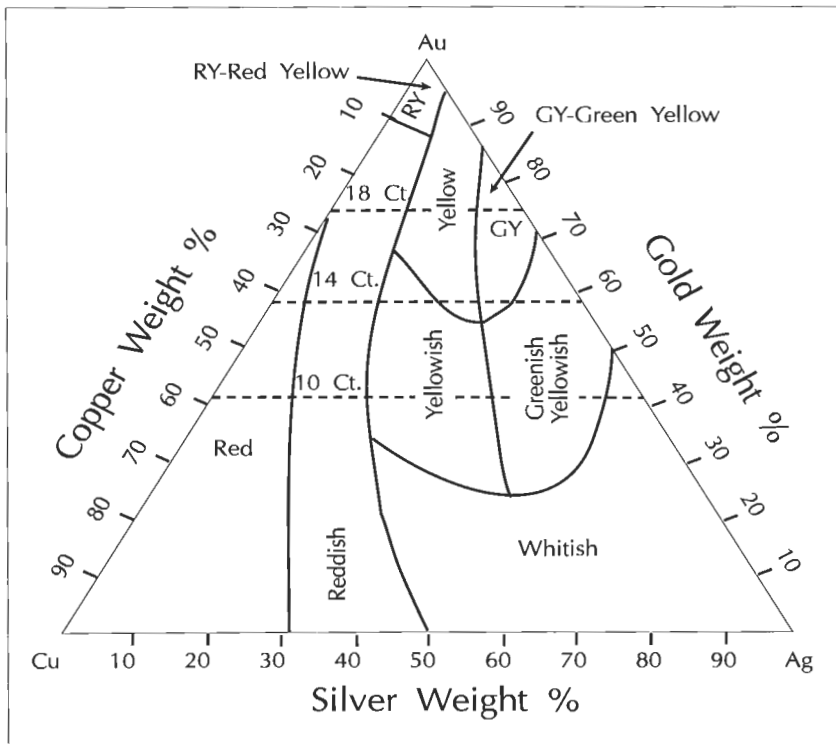
Figure 2

*Relationship between the colour and composition
of gold-silver-copper alloys. After [3].*

The authors then proceeded to show that Au-Ag-Cu (and Au-Ag-Cu-Zn) alloys can be logically classified and discussed in terms of only two parameters, namely their caratage and Ag'.

Based on the solid-state immiscibility gap and on the value of Ag', three types of alloys were distinguished, namely:

— Type I, in which Ag' ranges from 0 to about 10 % or from about 90 to 100 %. Such alloys, as will be seen from **Figure 1**, exist as homogeneous solid solutions at all temperatures below the melting point. They are soft in the annealed condition and are not hardenable.

— Type II, in which Ag' is in the range from about 10 to 25 % or 75 to 90 %. These alloys exist as homogeneous solid solutions at temperatures above the immiscibility gap, but if they are slowly cooled to equilibrium at room temperature $\alpha_{(Ag-Au)}$ will precipitate in copper-rich alloys and $\alpha_{(Cu-Au)}$ in silver-

rich alloys. These type II alloys are moderately soft in the annealed condition but are age-hardenable on heat treatment.

— Type III, in which Ag' is in the range from about 25 to 75 %. Alloys of this type are also homogeneous solid solutions above the immiscibility gap, but if slowly cooled to equilibrium room temperature, they decompose into both $\alpha_{(Ag-Au)}$ and $\alpha_{(Cu-Au)}$. Alloys of this type are hard in the annealed condition. They harden significantly on air cooling and are difficult to quench. They are age-hardenable

Alloys Based on the Au-Ag-Cu-Zn System

The relationship between the colour and composition of Au-Ag-Cu alloys is illustrated in **Figure 2** [3]. The colours range from gold-yellow near the gold-rich corner, to silver-white near the silver-rich corner, to copper-red. This last colour dominates not only the copper-rich corner, but also most of the copper-rich and gold-rich side of the diagram. The fact that alloys in these red and reddish areas can be made yellowish by additions of zinc is exploited in practice. These additions, which may be up to 15 wt.%, tend to reduce the volume of solid state immiscibility in the ternary phase diagram [4]. They cause a narrowing and a reduction in height of the two-phase area on each of the constant gold content sections of the ternary diagrams as presented in **Figure 1**. The Au-Ag-Cu-Zn carat gold alloys tend to be softer than the corresponding types of Au-Ag-Cu alloys in both the annealed and precipitation hardened states.

Commercial Coloured Gold Alloys Based on the Au-Ag-Cu and Au-Ag-Cu-Zn Systems

These can now with advantage be discussed in terms of the McDonald and Sistare classification into types I, II and III described above.

14 Carat Coloured Alloys

Since useful 14 carat alloys can be made at all values of Ag', as is illustrated in Table 1, these will be discussed first. With all 14 carat alloys (see **Figure 1**), the immiscibility gap is well developed, but there is a substantial temperature range between the top of the gap and the solidus over which the alloys are homogeneous. This permits alloys at all values of Ag' to be homogenized at elevated temperatures and to be quenched as homogeneous solid solutions at room temperature.

The *hardness* of these quenched solid solutions varies with Ag'. It is lowest for type I alloys, increases throughout the Ag' range of type II alloys, and is high in type III alloys. The Ag-rich type I and II alloys are somewhat softer than the Cu-rich type I and II alloys.

The *workability* of the alloys is related to their hardness range (Table 2). Type I alloys are the most easily worked, but they do not age-harden and are hardenable only by cold working. Type II alloys are workable in the annealed state and can be precipitation hardened after fabrication. Type III alloys are the hardest and most difficult to work. They require careful quenching, and if quenching is not done rapidly and effectively, decomposition of their solid solutions and age-hardening will occur.

Annealing of the alloys should be possible (see **Figure 1**) at 650 °C and this is the case. All the alloys in this class can be recrystallized and homogenized at this temperature. In practice, however, with wrought material under-annealing may lead to survival of a directionality of properties in the cold worked and subsequently annealed alloys, while over-annealing will result in excessive grain growth and the risk of orange-peel effects arising in subsequent working. With castings being solution annealed for subsequent precipitation hardening, when the only objective is to put the alloy in solid solution form, higher temperatures and longer times may be used. In general, the annealing temperature recommended can be varied with Ag', being lowest for

Table 1
Composition of Some 14 Carat Gold Alloys Commonly Used for Jewellery Manufacture in North America

Alloy code	Composition, wt.%				Ag' %	Alloy type
	Au	Ag	Cu	Zn		
110	58.3	4.6	36.9	0.2	11	I
220	58.3	9.1	32.4	0.2	22	II
310	58.3	12.9	28.6	0.2	31	III
400	58.3	16.5	25.0	0.2	40	III
600	58.3	24.8	16.8	0.2	60	III
750	58.3	31.0	10.5	0.2	75	III
780	58.3	32.5	9.0	0.2	78	II
850	58.3	35.0	6.5	0.2	84	II
116	58.3	4.0	31.3	6.4	11	I
224	58.3	8.3	29.2	4.1	22	II

type I, intermediate for type II and highest for type III alloys.

In **Figure 3**, the hardness values after annealing and water quenching and the maximum hardness values after heat treatment for the alloys listed in **Table I**, as plotted by McDonald and Sistare against Ag′ are presented.

A comparison of this with the 14 carat section in **Figure 1** demonstrates how well the concept of Ag′ imposes order on 14 carat Au-Ag-Cu jewellery alloys.

The hardness values for alloys 110, 116 and 224 also

Table 2

Rockwell Superficial Hardness (HR45T) of Some 14 Carat Coloured Gold Alloys as Annealed and in the Precipitation Hardened Conditions

Alloy	Annealed Condition	Hardened condition after annealing and quenching HR45T		
		Hardening temperature		
code	HR45T	205 °C	260 °C	315 °C
110	38-40	42-48	45-46	42-43
220	47-51	68-69	75-76	75-76
310	53-63	73-74	75-76	75-76
400	58-71	70-74	71-73	74-75
600	58-69	70-71	71-72	74-75
750	49-68		68-69	71-72
790	43-53		65-66	68-69
850	34-38		60-62	64-65
116	25-28	32-33	27-28	33-36
224	40-43	65-67	71-72	60-61

Specimens: 50 x 13 x 0.8 mm, cold rolled 50 % prior to annealing. Annealing time and Temperature: 30 min at 650 °C. Hardening time: 2-4 h.
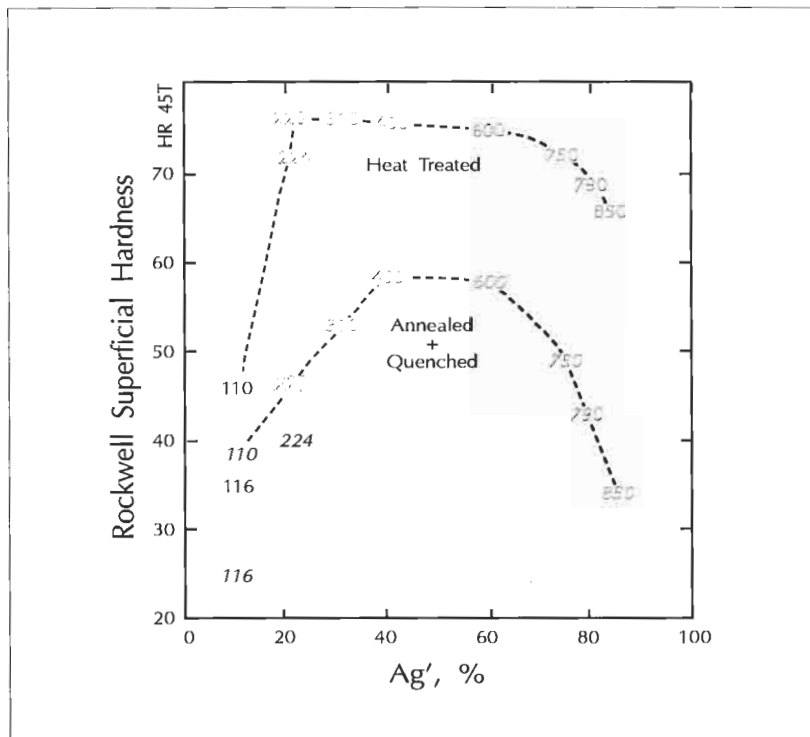

Figure 3

Rockwell superficial hardness (HR45T) of 14 carat commercial gold alloys in the annealed and quenched and the heat treated conditions as a function of Ag′. The alloys are coded as in Tables 1 and 2.

illustrate the softening effect of zinc additions to these alloys previously referred to.

10 Carat Coloured Alloys

From **Figure 1** it will be seen that the immiscibility field is broader and higher for 10 carat than it is for 14 carat alloys. In general, however, it will be noted that 10 and 14 carat alloys with Ag′ values in the type I, II and III ranges of composition respectively occupy corresponding positions in the 10 and 14 carat quasi-binary sections of the Au-Ag-Cu phase diagram (see **Figure 1**). It follows that there should be a correspondence between the metallurgical properties of 10 and 14 carat alloys with the same Ag′ values, and with certain exceptions, this is the case. Such alloys have been described as having 'associated' alloys compositions.

One source of exceptions can be illustrated by reference to **Figure 4**, which

is a projection on the room temperature plane of the Au-Ag-Cu phase diagram of some isothermal solid state boundaries of the immiscibility field. 'Associated' alloy compositions characterized by a particular value of Ag' all fall on a line which may be imagined as joining the gold corner of the diagram to a point on the Ag-Cu base corresponding to this value of Ag'. If such a line falls outside the immiscibility gap at 14 and 10 carat levels of gold content, then the properties of the associated alloys will be the same at both caratages. This means that they will be relatively soft homogeneous solid solutions and not age-hardenable. They will both be typical type I alloys. If, however, the constant Ag' line falls inside the immiscibility gap at both 10 and 14 carat compositions, it will be further inside this gap in the case of the 10 carat alloy than in the case of the 14 carat alloy, because of the greater width of the gap at the 10 carat level (see **Figure 1**).

The effect of this depends on the value of Ag' and therefore on the type of the alloy. Type III alloys which are well inside the immiscibility gap at both caratages tend to have similar properties at both caratages. However, at 10 carat they are harder and more difficult to anneal and quench than at 14 carat and find little application. In the case of 'associated' type II alloys marked differences can occur. Thus an alloy just inside the immiscibility field at 14 carat, will be capable of only moderate precipitating hardening, whereas its 'associated' 10 carat alloy may be well inside the field and precipitation harden to a significant degree. Such displacements relative to the immiscibility field will also give rise to differences in other characteristics of the associated alloys such as solutionizing, processing and optimum precipitation temperatures, optimum ageing time and susceptibility to overageing and softening.
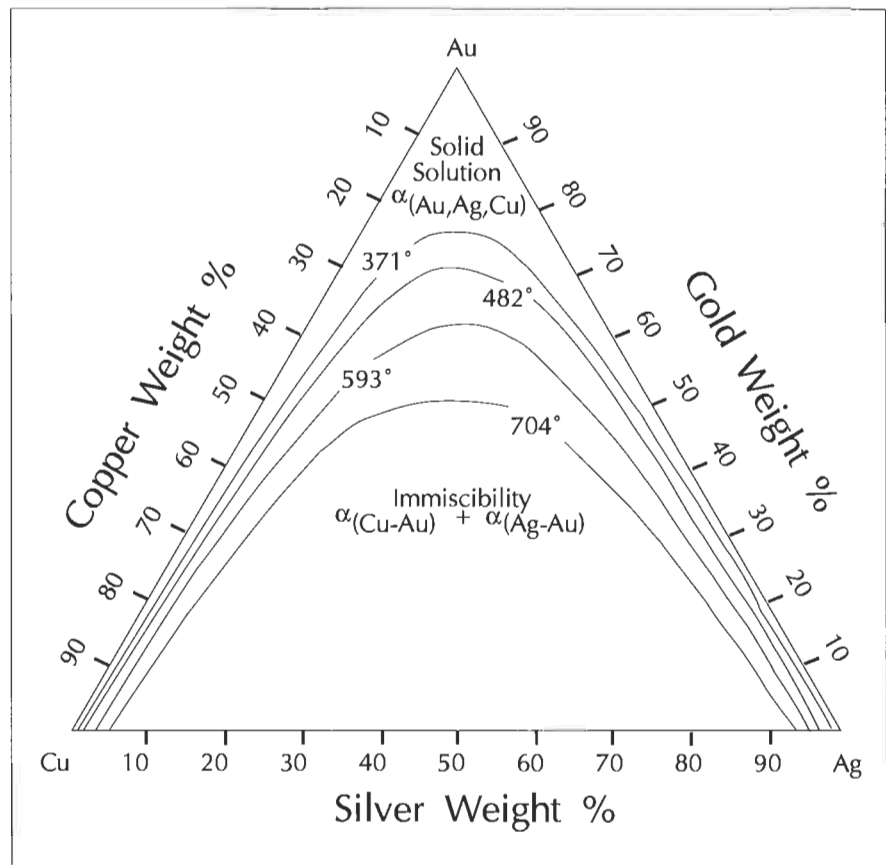

Figure 4

Projection on the room temperature plane of the gold-silver-copper ternary phase diagram of some isothermal solid state boundaries of the immiscibility field.
After [25].

A second reason for exceptions in respect of the expected correspondence between 'associated' 14 and 10 carat alloys may be the effect of the zinc added to many of these alloys. This tends to reduce the volume of the immiscibility field and moreover the absolute zinc content increases in the 10 carat alloys in which the same relative proportions of silver, copper and zinc are maintained.

In spite of these exceptions, the extent of the correspondence between the expected properties of 10 carat alloys and those of their associated 14 carat alloys is remarkable. For example the following are the compositions of three typical commercial 10 carat gold jewellery alloys which have the same Ag' values as the 14 carat alloys 116, 224 and 850 listed in **Table 1**:

Code	Au	Ag	Cu	Zn	Ag'%	Type
119	41.7	5.50	43.8	9.0	11	I
226	41.7	11.70	40.8	5.8	22	I
840	41.7	48.90	9.05	0.35	84	II

The 'associated' type I 14 and 10 carat alloys (Codes 116 and 119) have mechanical properties so nearly the same that they can be processed in essentially the same way. The type II 14 and 10 carat alloys, however, show significant differences in behaviour. These can be attributed in the case of the one pair (14 carat code 224 and 10 carat code 226) to the fact that the 14 carat alloy falls only just inside the immiscibility field with the result that the 'associated' 10 carat alloy is well within this field, with the consequences described above. In the case of the other pair (14 carat code 850 and 10 carat code 840) the differences are due to the net effects of shifts in the solid solution boundary in converting from 14 carat to 10 carat on the one hand and on the other hand to the reduced volume of the immiscibility field resulting from the increase in absolute zinc content of the 10 carat alloy as compared with that of its 'associated' 14 carat alloy.

18 Carat
Coloured Alloys

The concept of alloy types, which is so useful in discussing 14 carat and 10 carat alloys is much less useful with 18 carat alloys. Thus the immiscibility field occupies a much smaller area of the solid state field in these alloys than it does in the alloys of lower caratages. Moreover the Au-Cu ordered phase of the Au-Cu binary system occupies part of this field (**Figure** 4 and reference). One effect of this is that, for example, a copper-rich alloy in the Ag' range of composition corresponding to type I, and which would be soft and not age-hardenable at 10 and 14 carat, is hardenable at 18 carat due to the influence of the Au-Cu ordered phase. Another effect is that alloys in the Ag' range corresponding to type III, which are all hard at 10 and 14 carat, are only moderately hard and age-hardenable at 18 carat, because of the restricted area of the immiscibility field. They tend to resemble type II 14 carat and 10 carat alloys. Above an Ag' value of 75 %, moreover, 18 carat alloys are soft and non-hardenable.

Coloured Alloys
of Caratages Greater than 18

Above 18 carat, the concept of types is not applicable. In this range, Au-Ag-Cu alloys, both annealed and heat treated, are progressively softer with increasing gold content. Their properties approach those of 24 carat or pure gold, and they find little application except in the production of gold coins and medallions, for which alloys of fineness 900 (21.6 carat) and 916.66 (22 carat) are widely used. Because of their relative softness and their relative susceptibility to scratching and wear, they have not been greatly used in fabrication of jewellery, other than wedding rings. It is because of these facts that the introduction of the new 990 gold-titanium alloy, with a caratage of 23.76, is so significant.

Alloy Data in Respect of
Commercial Coloured Carat Gold Alloys
Based on the Au-Ag-Cu and
Au-Ag-Cu-Zn Systems

As a result of cooperation between the International Gold Corporation Ltd., Degussa AG, Johnson Matthey Metals Ltd. and Métaux Précieux SA Metalor, technical data in regard to a number of standard coloured carat gold alloys widely used in jewellery fabrication, especially in Europe, have become available in recent years. The alloys for which such data are available are the following:

Alloy *	Designation	Reference
23.76 carat		
Au 990-Ti 10	990 Gold Titanium (yellow)	17
22 carat		
Au 917-Ag 32-Cu 51	22 LS (dark yellow)	12
Au 917-Ag 55-Cu 28	22 LS (yellow)	14
18 carat		
Au 750-Ag 125-Cu 125	750 Y-3 (yellow)	5
Au 750-Ag 160-Cu 90	750 Y-2 (pale yellow)	6
Au 750-Ag 90-Cu 160	750 Y-4 (pink)	7
Au 750-Ag 45-Cu 205	Au 750 S (red)	8
14 carat		
Au 585-Ag 265-Cu 150	Au 585 S (pale yellow)	9
Au 585-Ag 205-Cu 210	Au 585 S (yellow)	1
Au 585-Ag 90-Cu 325	Au 585 S (red)	11
Au 585-Ag 100-(Cu-Zn) 315	585/100 (pink)	13
Au 585-Ag 300-Cu 115	585/300 (yellow)	15

9 carat
    Au 375-Ag 100-Cu 450-Zn 75   375 DF (yellow)   16

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* Similar alloy data have also been published in respect of 18 and 14 carat white gold alloys [18-22].

The 990 (23.76 carat) Gold-Titanium Alloy

Metallurgical and Physical Properties

In comparison with the metallurgy of the traditional Au-Ag-Cu and Au-Ag-Cu-Zn carat gold alloys, that of 990 Au-Ti is relatively simple. The phase diagram for the Au-Ti system was recently assessed by Murray [23] and the portion of it which is relevant, namely that for the composition range 85 to 100 wt.% Au is presented in **Figure** 5. It will be seen that the solubility of Ti in solid gold falls steadily below the peritectic temperature of 1123 °C as a result of the separation of TiAu$_4$. Gafner [1] has reported the solubility as falling from 1.2 wt.% at 800 °C to 0.4 wt.% at 400 °C. The 990 Au-Ti alloy (1 wt.% Ti) therefore becomes solutionized at 800 °C, and on cooling from this temperature to 400 °C it hardens significantly, because of the relatively high volume of the compound (TiAu$_4$) in which the Ti separates.

The behaviour of the alloy on solutionizing, cold working and age-hardening has been reported upon as well as the mechanical properties of the alloy on solutionizing and quenching, on cold working, and on age-hardening for different times at 400, 500 and 600 °C [1]. These properties are comparable with the corresponding properties of conventional 14 and 18 carat coloured alloys in similar states. Of special interest is the fact that the 990 alloy retains enough ductility after hardening for rings fabricated from it to be adjusted in size. Moreover the cold worked alloy has a hardness of 120 HV, which is an ideal value for coins for striking. Coins and medallions can therefore be produced in this alloy without any annealing step between strip rolling and blanking.

Hardening for one hour at 500 °C gives the alloy a hardness of 240 HV and a tensile strength of 740 MPa, which are comparable with the values for these proper-

ties which are observed with conventional alloys hardened by high concentrations of copper. In this state the alloy has proved suitable for lathe turning using diamond tools for ring and bangle production. Grain size calls for the same attention in the 990 Au-Ti alloy as it does in conventional alloys, though no cases of orange peel effects associated with materials of large grain size have so far been observed. An alloy containing Au 990; Ti 9.1; Ru 0.5; and B 0.4 ‰ has been observed to yield castings of greatly improved texture. The 990 Au-Ti alloy exhibits a dramatic improvement in grain size following age-hardening of 70 % deformed material at 500 °C. In respect of its physical properties and metallurgical behaviour this new alloy therefore presents few problems to those familiar with conventional coloured gold alloys. It does, however, have chemical properties which call for special attention.
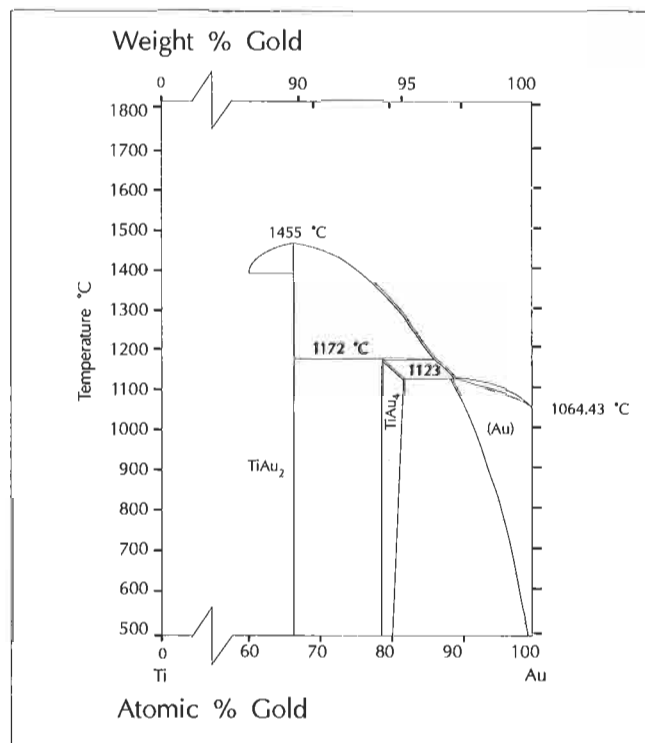

Figure 5

The assessed Au-Ti phase diagram for the composition range 85 to 100 wt.% Au. After [23].

Chemical Properties

Titanium reacts with both oxygen and nitrogen at elevated temperatures. As a result tarnish develops on the surface of the alloy when exposed to air under these conditions, and in the process titanium is lost from the alloy. As a result:

— Production of the alloy must be carried out in a vacuum in an induction furnace back-filled to at least 1 torr with pure argon.

— During procedures such as solutionizing, age-hardening, soldering and brazing, precautions must be taken to minimize its exposure to air. This can be done without recourse to vacuum equipment or protective atmospheres during most procedures. For example, solutionizing and heat treating can be carried out at the recommended temperatures of 800 °C and 500 °C respectively in molten salt baths. Similarly, the alloy can be protected during soldering and brazing by the use of fluxes. Not all salt baths or fluxes are suitable, however, since some attack the titanium in the alloy. Materials found suitable include B_2O_3 and Degussa 540 salt for solutionizing at 800 °C, Degussa 430 salt and Flux-h for heat treating at 500 °C, and Degussa Fluxes -t or -L or Canning for soldering or brazing.

— The tarnish which forms on the alloy at elevated temperatures is different from that which develops on conventional alloys. It can be effectively removed by dipping the article into a 10 % solution of potassium pyrosulphate ($K_2S_2O_7$), drying, and then heating until the residual $K_2S_2O_7$ melts. On quenching and washing the alloy is obtained tarnish-free.

— Not all crucible materials are suitable for use with the 990 alloy. Suitable materials are alumina, zirconia and high-purity carbon.

— Investment casting of the alloy can present problems. At present too few casting tests have been carried out for it to be classified as a casting alloy.

Refining

As a by-product of the search for suitable salts and fluxes for use with the alloy, it was found that Degussa salt 560 removes the titanium from the alloy when it is melted with it at 1100 °C. Refining of scrap alloy to a fineness of 999.8 is achieved in 20 minutes at this temperature. This means that 990 Au-Ti scrap can be easily and rapidly refined to a state where it can be directly used for making a further batch of the alloy. □

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ABSTRACTS
&
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Selected from
current scientific and technical literature on gold

The abstracts published here have been specially written for *Gold Bulletin* and, in contrast to conventional abstracts, usually include some background information about the subject of the abstracted paper. Authors of scientific or technical articles relating to gold or its industrial uses are invited to forward reprints of their papers to *Gold Bulletin*, together with an extended abstract for speedy publication in this section.

MATERIALS & PROPERTIES

A 90 4 125

Standard of Specular Reflectance at Near Normal Incidence for the Infrared Region

The development of a specular reference standard at near normal incidence for the 2.5-25 µm region of the infrared is described. The materials used were aluminium, gold and silicon. The gold standard was made by vapour depoposition of the metal on an optically flat, polished and clean glass surface. No protective coating was applied. Computed and experimentally observed specular reflectance values for gold are recorded.

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Atomic Short-Range-Order Structure in Gold-Iron Alloys

It was reported in 1989 by Yoshida, Langmayr, Fratzl and Vogl, on the basis of high temperature Mössbauer spectroscopy and small-angle X-ray scattering experiments, that clustering of Fe atoms does not occur in Au-Fe alloys containing 1-15 at.% Fe. Contrary to this finding the authors of this paper conclude, on the basis of TEM, small angle scattering and X-ray diffuse scattering analyses of Au75Fe25 and Au80.9Fe19.1 alloys, that the cluster model provides the most plausible explanation of the various structural and magnetic observations made on alloys in the Au-Fe system.

This conclusion is relevant to our understanding of the spin glass or micromagnetic behavior of Au-Fe alloys (and other alloys in which a magnetic soluble is in solution in a non-magnetic solvent metal). This aspect is reviewed in some detail by the authors.

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