The Metallurgy of Some Carat Gold Jewellery Alloys

PART I — COLOURED GOLD ALLOYS

Allen S. McDonald and George H. Sistare

Handy & Harman, Fairfield, Connecticut, U.S.A.

The classification of gold alloys in terms of caratage and colour provides no guidance as to the properties and working characteristics of the many carat gold alloys used in jewellery fabrication. Logical relationships do exist, however, between the composition, metallurgical structure and properties of such alloys, and these emerge from a study of the phase diagrams of the alloy systems involved. Part I of this review deals with coloured gold alloys. Part II will discuss their nickel containing counterparts and will appear in the next issue of Gold Bulletin.

Most carat gold for jewellery falls into one or other of two major categories, the coloured gold alloys based on the gold-silver-copper or the gold-silver-copper-zinc system and the white gold alloys.

Although many coloured gold alloys contain zinc (from less than 1 to about 15 weight per cent), it is valid to introduce this group in terms of the gold-silver-copper ternary system, from which all of the alloys inherit certain fundamental metallurgical characteristics. After establishing these, the effects of zinc will be introduced, and it will then be seen that in the amounts used this element does not change these characteristics in kind but rather interacts to modify them in a regular and symmetrical way.

Figure 1 presents the gold-copper, copper-silver and silver-gold binary phase diagrams (1). The ternary phase diagram can be established by progressively adding gold to the copper-silver system. One might expect a liquidus valley to extend from the copper-silver eutectic point at 780°C to the gold-copper liquidus minimum at 911°C. This valley exists and is shown in Figure 2. One might also expect the solid state immiscibility field in the copper-silver system to intrude into the ternary diagram to a considerable extent. Indeed it does, shrinking laterally and vertically, as compositions approach the gold corner. This is illustrated in Figure 3, where the solid state isothermal boundaries of the immiscibility field have been projected onto the room temperature plane. The existence of this immiscibility field is by far the most important factor in determining the basic metallurgical characteristics of the coloured jewellery gold alloys.

Three quasi-binary vertical sections of the ternary diagram at constant gold contents characteristic of jewellery alloys (10, 14 and 18 carat) are schematically represented in Figure 4 where the parameter used on the abscissa is defined as:

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

Gold-silver-copper and gold-silver-copper-zinc alloys can be logically classified and discussed in terms of two parameters, namely the caratage or gold content and Ag' .

Given constant gold content sections of the ternary diagram, for example the 14 carat section in Figure 4, the concept of three 'types' of alloy based on the immiscibility gap and defined by values of Ag' can be introduced.

Type I where Ag' ranges from 0 to about 10 per cent or from about 90 to 100 per cent. These alloys exist primarily as homogeneous solid solutions at all temperatures below the melting point. Alloys of this type are soft in the annealed condition and are not age-hardenable.

Type II where Ag' is in the range from about 10 to 25 per cent or 75 to 90 per cent. These alloys will exist as homogeneous solid solutions at temperatures above the immiscibility gap, but if slowly cooled to equilibrium at room temperature $\infty_{(Ag-Au)}$ will precipitate in copper-rich alloys and $\infty_{(Cu-Au)}$ in silver-rich alloys. Type II alloys are moderately soft in the annealed condition but are age-hardenable by heat treatment.

Fig. 1 Gold-copper, copper-silver and silver-gold binary phase diagrams. On the gold-copper diagram, note the minimum liquidus temperature and the existence of two ordered phases, AuCu and AuCu₃. The copper-silver diagram shows that due to the eutectic decomposition of the homogeneous liquid phase into copper-rich and silver-rich phases, binary alloys are two-phase in the solid state except when either of copper or silver is present in a very small quantity only. Silver-gold binary alloys are single phase at all concentrations. After (1)

Fig. 2 Projection on the room temperature plane of the gold-silver-copper ternary phase diagram of some isotherms on the liquidus surface. A liquidus valley extends from the silver-copper eutectic point to the gold-copper liquidus minimum. After (1)

Fig. 3 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 (1)

Fig. 4 Schematic quasi-binary sections at constant caratage of the gold-silver-copper ternary phase diagram. The parameter Ag' is defined in the text

Fig. 5 Relationship between the colour and composition of gold-silver-copper alloys. After (2)

Type III where Ag' is in the range from about 25 to 75 per cent. These alloys are homogeneous solid solutions at temperatures above the immiscibility gap, but if slowly cooled to equilibrium at 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 markedly during air cooling and are difficult to quench. Type III alloys are age-hardenable.

In the jewellery industry, alloys are usually classified in terms of caratage and colour rather than of metallurgical properties. The hue of gold-silver-

copper alloys could be expected to range from 'copper-red' near the copper-rich corner, to 'gold-yellow' near the gold-rich corner, to 'silver-white' near the silver-rich corner. A more precise delineation (2) of the actual colour fields is illustrated in Figure 5.

It will be noted in Figure 5 that 'copper-red' dominates not only the copper-rich corner but most of the copper- and gold-rich side of the diagram. Alloys in these red and reddish areas can be, and are, made yellowish by an addition of zinc.

The effect of zinc on the concept of alloy types as defined above, will be understood if it is borne in mind that the addition of this element tends to reduce (3) the volume of solid state immiscibility in the ternary phase diagram.

The small amounts of zinc (about 0.5 per cent or less) added as a deoxidizer in 10 and 14 carat alloys have no significant effect on the metallurgical characteristics under discussion. Larger additions (up to about 15 weight per cent) are, however, used to change the red colour of low and middle caratage copper-rich alloys to reddish yellow or dark yellow. These soften the alloys in both the annealed and precipitation hardened state. This is a consequence of the narrowing and reduction in height of the two phase area on each of the constant gold content sections of the ternary diagram shown in Figure 4.

These general concepts will aid a survey of some commercial alloys. For this purpose, the reader will

find it useful to imagine the metallurgical concept of alloy types as a grid that may be superimposed on the colour diagram of Figure 5. Thus the jeweller's classification of alloys based on caratage and colour can be translated into the present metallurgical classification based on caratage and Ag' values.

14 Carat Coloured Alloys

A survey of commercial gold alloys will best begin with alloys of intermediate caratage because at 14 carat useful alloys can be made at all values of Ag' . On the 14 carat section in Figure 4, although the immiscibility gap is well developed, there is a substantial homogeneity temperature range between the top of the gap and the solidus. This permits alloys at all values of Ag' to be homogenised at elevated temperature and to be quenched as homogeneous solid solutions at room temperature. In this quenched or solid solution condition, the hardness varies with Ag' , being lowest for type I alloys, increasing rapidly throughout the Ag' range of type II alloys, and is high in type III alloys. Silver-rich type I and II alloys are somewhat softer than copper-rich type I and II alloys.

Workability is essentially related to the hardness range. Type I alloys are the most easily worked. However, they are not hardenable except by cold-working. Type II alloys are more versatile. They are workable in the annealed state and can be precipitation hardened after fabrication. In special cases where maximum hardness is required (gold pen nibs for instance), type III alloys are available. These alloys are complex to process. They are the hardest and most difficult to work. They require careful quenching, and if not quenched rapidly and effectively, decomposition and resulting hardening will occur.

Examples of 14 carat alloy compositions are given in Table I. Most of the compositions discussed here are commercial alloys that have been, or are currently popular in North America. The particular compositions used in various parts of the world depend to a large extent on local hall-marking laws and colour preferences. Proprietary names have been avoided and the alloys in Table I are designated by code numbers and arranged in order of increasing Ag' and zinc content. These two factors together with caratage largely specify the metallurgical nature of each alloy. Table II lists Rockwell superficial hardness values (HR45T) in the annealed and heat treated conditions. The values were determined on wrought samples 63×13 mm, deformed 50 per cent by cold-rolling to 0.8 mm gauge. All samples were annealed at 650°C for 30 minutes. This treatment led to standard reference conditions for all the alloys, from which comparative hardenability studies were undertaken.

It should be emphasized at this stage that in shop production, it is usually necessary to select the anneal-

ing schedule best suited to each particular alloy. For example, annealing at 650°C is sufficient to both recrystallise and homogenize all of the alloys under discussion. In practice, however, with wrought material, one needs to steer clear of both the Scylla and Charybdis of gold jewellery annealing for subsequent forming — the directionality of properties associated with under-annealing, and the orange peel effects associated with over-annealing. On the other hand, when solution annealing castings for subsequent precipitation hardening where the only objective is to put the alloy into solid solution, one leans in the direction of relatively higher temperatures and longer times. In general, the annealing temperature recommended for shop practice varies with Ag' , being lowest for type I alloys, intermediate for type II, and highest for type III.

The hardness values reported in Table II for annealed samples cover the range that can be expected in practice depending on whether or not the alloy is adequately quenched. The lower value in the range can be attained if the alloy is quenched in water. The higher value may result if the alloy is cooled in air. The range of hardness values for type III alloys vividly illustrates the necessity of fast quenching when these alloys are process annealed for subsequent working.

The hardness values after heat treatment reported in Table II were determined on samples solution annealed at 650°C for 30 minutes and water quenched prior to hardening at the indicated temperature for 2 to 4 hours.

The hardness values after annealing and water quenching and the maximum hardness values after heat treatment which are listed in Table II have been plotted against Ag' in Figure 6. A comparison of this plot with the 14 carat section in Figure 4, shows how well the concept of Ag' imposes order on 14 carat jewellery gold alloys. The relationship between composition, hardening characteristics, and the phase structure of the alloy system is quite symmetrical. The relationship is further illustrated in Figure 7, which shows the metallographic structures of the series of alloys coded 110 to 840 (see Table I). These structures were developed by annealing at 650°C for 1 hour and slow overnight cooling in the furnace. Water quenched samples of the same alloys all had homogeneous solid solution structures. The varying amount of precipitation and decomposition which can take place as compositions shift across the immiscibility field from the copper side to the silver side with increasing Ag' is clearly evident.

Comparing the hardness values of alloy 110 (11 per cent Ag' , 0.2 per cent zinc) in the quenched and the hardened conditions with those of alloy 116 (11 per cent Ag' , 6.4 per cent zinc) and the values of alloy 220

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

Alloy code	Composition, wt. per cent				Ag' per cent	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

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

Alloy code	Annealed condition HR45T	Hardened condition after annealing and quenching HR45T		
		Hardening temperature		
		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 × 13 × 0.8 mm, cold rolled 50 per cent prior to annealing. Annealing time and temperature: 30 minutes at 650°C. Hardening time: 2 to 4 hours

(22 per cent Ag', 0.2 per cent zinc) with those of alloy 224 (22 per cent Ag', 4.2 per cent zinc) in Table II and Figure 6, illustrates the softening effect of zinc additions which was previously referred to.

10 Carat Coloured Alloys

A comparison of the 10 and 14 carat sections in Figure 4 shows a broader and higher immiscibility field at 10 carat. A 14 carat alloy with a particular value of Ag' can be converted into its 'associate' 10 carat alloy by reducing the gold content while maintaining the same relative proportion of other alloying elements and thus maintaining the same value of Ag'.

Fig. 6 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 I and II

A) Alloy 110, $Ag' = 11\%$, type I

B) Alloy 220, $Ag' = 22\%$, type II

C) Alloy 310, $Ag' = 31\%$, type III

D) Alloy 400, $Ag' = 40\%$, type III

E) Alloy 600, $Ag' = 60\%$, type III

F) Alloy 750, $Ag' = 75\%$, type III

G) Alloy 780, $Ag' = 78\%$, type II

H) Alloy 850, $Ag' = 84\%$, type II

Fig. 7 Equilibrium microstructures developed in 14 carat alloys 110 to 850 (see Table I) by annealing at 650°C for 1 hour and slow overnight cooling.

A: Homogeneous copper-rich solid solution

B: Homogeneous copper-rich solid solution with silver-rich second phase precipitates at the grain boundaries

C and D: Immiscible copper-rich and silver-rich phases

E to H: Homogeneous silver-rich solid solution with copper-rich second phase precipitates at the grain boundaries

Under these conditions, an alloy of a given type (in the sense defined earlier) at 14 carat will generally convert to an alloy of the same type at 10 carat. However, in some cases the properties of an alloy converted from 14 to 10 carat may be significantly altered, depending on the particular value of Ag' . It can be seen how this takes place by considering Figure 3 and imagining lines dropped from the gold corner to particular values of Ag' on the silver-copper base. All 'associated' alloy compositions falling on a particular line have the same value of Ag' . If such a line falls outside the immiscibility field at 14 and 10 carat, the properties of the associated alloys will be very similar at both caratages. They will be relatively soft homogeneous solid solutions and not precipitation hardenable. This is the case for type I alloys. If the constant Ag' line falls inside the immiscibility field at both caratages, it is always the case that it is farther inside the field at 10 carat than at 14 carat because the immiscibility field is broader at 10 carat than at 14 carat. How this effects changes in properties depends on the range of Ag' . Type III alloys, which are well inside the immiscibility field at both caratages tend to have similar properties at 10 and 14 carat. However, at 10 carat they are much harder and much more difficult to anneal and quench than at 14 carat. Marked differences can occur in the conversion of type II alloys. In this range, a yellowish alloy or a greenish alloy 'just inside' the immiscibility field at 14 carat and capable of only moderate precipitation hardening may, on conversion to 10 carat be 'well inside' the field and precipitation harden to a significant degree. Such displacements relative to the immiscibility field will also affect the process annealing, solution annealing and optimum precipitation hardening temperature, optimum ageing time, and susceptibility to overageing and softening. Alloy additions of zinc also have an effect in changing properties on converting between 14 and 10 carat because zinc tends to reduce the volume of the immiscibility field, and the absolute zinc content increases with conversions which maintain the same relative proportions of the alloying elements (silver, copper, and zinc).

At 10 carat, type III alloys are not in general use because they are too hard and difficult to anneal for practical fabrication and their colour is not attractive.

The compositions (weight per cent) of three typical commercial 10 carat jewellery gold alloys are listed below:

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	II
840	41.7	48.90	9.05	0.35	84	II

These alloys are based on the conversion of 14 carat alloys 116, 224, and 850 listed in Table I and have

been arrived at as described above. The type I alloys (14 carat 116 and 10 carat 119) have mechanical properties so nearly the same at both caratages that they can be processed in essentially the same way. The type II yellow alloys (14 carat 224 and 10 carat 226) show significant differences between the two caratages. For example, 224 is solution annealed in 30 minutes at 650°C whereas 30 minutes at 705°C are required with 226. The optimum precipitation hardening schedule for 224 is ageing between 230 and 260°C for 2 to 4 hours, while 226 is aged at 315°C for 1 hour. Heat treatment of the 14 carat alloy at 315°C will result in overageing and softening while if the 10 carat alloy is treated at 260°C maximum hardness will not be obtained.

The maximum hardness of the two alloys after heat treatment is about 71 HR45T for 224 and 73 HR45T for 226. These differences are due primarily to the relative displacement of the solid solution boundary from the $Ag' = 22$ per cent line to the left in converting from 14 to 10 carat. However, alloy 224 which contains 4 per cent zinc converts into 226 with 6 per cent zinc. The additional 2 per cent of zinc at 10 carat shifts the solid solution boundary back to the right and therefore reduces the net displacements. The type II green alloys (14 carat 850 and 10 carat 840) also exhibit some interesting differences in properties. Again, the 14 carat alloy can be solution annealed at 650°C for 30 minutes, but with the 10 carat alloy 705°C for 30 minutes is required. Both can be precipitation hardened at 315°C — 850 in 2 hours and 840 in 2 to 4 hours. The maximum hardness of the 14 carat alloy in the heat treated condition is 65 HR45T, while it is 70 HR45T for the 10 carat alloy. The latter is so much further into the two phase region than the 14 carat alloy that it acquires one of the characteristics of type III alloys, namely, it is very susceptible to hardening on air cooling and must be effectively quenched on annealing if subsequent forming operations are intended.

18 Carat Coloured Alloys

On the 18 carat section in Figure 4 it will be noted that the immiscibility field occupies a much smaller area of the solid state field than at lower caratage. Also, the AuCu ordered phase of the gold-copper binary system intrudes into the ternary field. The concept of alloy types used above in discussing 10 and 14 carat alloys is far less useful at 18 carat. For example, a copper-rich alloy in the Ag' range corresponding to type I, which would be non age-hardenable and soft at 10 and 14 carat, is hardenable at 18 carat due to the effect of the AuCu ordered phase. 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 due to the restricted area of

the immiscibility field, and behave more like type II alloys do at 10 and 14 carat. Soft and non age-hardenable alloys are found in the range of Ag' greater than about 75 per cent. Above 18 carat, the concept of type is not practically useful at all. In this range, the alloys both annealed and heat treated are progressively softer with increasing gold content and approach the properties of 24 carat or pure gold.

If one refers to the colour diagram in Figure 5, and imagines lines drawn from the gold corner through the intersection of the colour boundaries with the 18 carat line and then continued to the Ag' values on the silver-copper axis it can be seen that at 18 carat, red gold alloys occur in the Ag' range 0 to about 40 per cent, yellow alloys in the Ag' range 40 to 80 per cent, and green alloys in the Ag' range from about 80 to 100 per cent. If one now observes where these ranges fall on the 18 carat quasi-binary section in Figure 4, the following generalisations can be made:

All 18 carat green alloys behave like type I soft and non-precipitation hardenable alloys because their compositions fall well outside the immiscibility field. There are no type I red alloys at 18 carat because at low values of Ag' the ordering of the AuCu phase is available as a hardening mechanism. Yellow alloys at

18 carat fall within the Ag' range of type III alloys at 10 and 14 carat, but behave like 14 carat type II alloys do as indicated above.

The compositions (weight per cent) of three typical 18 carat jewellery alloys are listed below:

Colour	Code	Au	Ag	Cu	Ag'%
Red	200	75	5	20	20
Yellow	600	75	15	10	60
Green	900	75	23	2	90

The red alloy 200 responds to hardening on heat treating (75 HR45T after solution annealing at 595°C followed by hardening at 260°C for 2 hours), although its position at 20 per cent Ag' in the 18 carat section of Figure 4 suggests that it might fall outside the influence of both the ordered field and the immiscibility gap. The yellow alloy 600 can be treated to 66 HR45T by solution annealing at 650°C followed by precipitation hardening at 260°C for 2 hours. The green alloy 900 is not precipitation hardenable.

References

- 1 'Metals Handbook', 8th edition, vol. 8, American Society for Metals, Metals Park, Ohio, 1973
- 2 J. Leuser, *Metall*, 1949, **3**, 105-110, 128
- 3 C. McCaul, R. Krahn and C. d'Antonio, *Trans. Am. Inst. Min. Metall. Eng.*, 1969, **245**, 432-434

The second part of this article will be published in the October 1978 issue of Gold Bulletin.

The Thermal Conductivity of Gold

In low temperature equipment, thermal contact between solid state devices, thermometers etc. and the surroundings may be limited by the conductance of thin gold wires between them. Prediction of the thermal conductivity of such wires at low temperatures is therefore of importance. As a result of measurements reported by V. Novotny from the Department of Physics at the University of Toronto (1), such prediction is now possible.

The conduction of heat in gold is due almost exclusively to electrons, since phonons are effectively scattered. This means that the two conduction processes – electrical and thermal, are very similar. In fact there exists a very simple relationship between the two, the Wiedemann-Franz (WF) law, established over a hundred years ago. This is

$$\lambda/\sigma T = L_0$$

where λ is the thermal conductivity
 σ is the electrical conductivity

T is the absolute temperature in degrees K

and L_0 is the Lorenz number, which is a constant of value $2.45 \times 10^{-8} \text{ W}\Omega/\text{K}^2$. Since the electrical conductivity is much easier to measure, one may derive the thermal conductivity of a metal from the above equation, provided that no deviations from the WF law occur.

The WF law has been established, however, on the basis of elastic scattering. Although this is a good approximation for gold at temperatures below 10 K and above 300 K, between these temperatures the ratio $\lambda/\sigma T$ decreases, depending on sample purity. In pure metals, deviation arises from non-elastic electron-phonon

scattering processes which generally show up between θ_D (the Debye temperature, which for gold is about 190 K) and $\theta_D/30$. In impure metals, deviation arises from the presence of minute amounts (~ 10 ppm) of magnetic impurities (iron, chromium, manganese).

Since at very low temperatures the electrical conductivity of pure metals is constant ('residual resistivity'), the thermal conductivity should be proportional to temperature. This is actually observed, with $\lambda = \alpha T$ where $\alpha = \sigma T L_0$. Where deviations due to the failure of the WF law occur, this relationship does not hold, and the thermal conductivity at low temperature can be written as

$$\lambda = \alpha T + \beta T^2 + \gamma T^3 + \dots$$

where β and γ are small.

Commercial gold wires are normally made from high purity gold, and Novotny found for the sample (diameter $51 \pm 1 \mu\text{m}$; 99.7 per cent gold) studied by him that the thermal conductivity was given by

$$\lambda = 0.117 T + 7 \times 10^{-4} T^2 \quad (\text{WK}^{-1}\text{cm}^{-1})$$

between 0.8 and 10 K.

The data agree within 20 per cent with those calculated from the measured residual electrical resistivity using the WF law. This implies that predictions of the thermal conductivity of other gold wires at low temperatures can be made to within engineering accuracy over a wide range of residual resistance ratios.

Reference

- 1 V. Novotny, *Cryogenics*, 1977, **17**, 451-452

J.K.