A Plain Man's Guide To Alloy Phase Diagrams: Their Use In Jewellery Manufacture - Part 2

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The first part of this paper, published in the previous issue of *Gold Technology*, described the construction of binary alloy phase equilibrium diagrams and explained how they may be interpreted in terms of alloy solidification and microstructure. This part goes on to describe the phase diagrams for ternary alloy systems and the use of phase diagrams in jewellery manufacture.

Ternary Phase Diagrams

Ternary alloy systems contain three component metals and the relevant ternary phase equilibrium diagram describes their alloying behaviour. These diagrams may contain any of the features discussed so far, such as single-phase solid solutions, miscibility gaps, binary eutectics, etc. Binary phase diagrams can never have more than two phases co-existing in equilibrium whereas up to three phases may co-exist in a ternary system. Consequently, it is possible to have diagrams with three-phase fields and ternary eutectics.

There are other important differences. Instead of a composition line axis, the composition of any alloy in the system has to be found on a two-dimensional horizontal base, which by convention is an equilateral triangle, Figure 23. The diagram for the ternary alloy system gold-silver-copper (Au-Ag-Cu) is a very good example to consider. Not only is it of relevance to jewellers, but it is reasonably easy to describe and it is often used in instructing students taking metallurgical qualifications.

The composition base

You will see that the corners of the triangle represent the pure metals at the 100% composition. The sides of the triangle give the composition axes for the binary systems, i.e. the side joining gold (Au) and silver (Ag) gives the compositions of all binary gold-silver (Au-Ag) alloys from 0 to 100 % silver. Similarly, the other two sides will give the binary systems compositions silver-copper (Ag-Cu) and gold-copper (Au-Cu). Again, compositions may be plotted either in terms of wt.% or at.%. It is convenient to relate compositions to caratage and for that reason we shall use wt.% unless stated otherwise.

If we plot the point 75% Au-25% Ag along the Au-Ag side of the triangle, we know that this will represent an 18 ct greenish-yellow gold. If we plot the point for 75% Au - 25% Cu along the Au-Cu side, this represents an 18 ct red gold. Joining the two 18 ct points across the triangle gives a line which represents all ternary 18 ct alloys with decreasing Ag and increasing Cu as we go from left to right. Intuitively, we should expect that selecting a point X halfway along this line will give a composition which contains equal amounts of Ag and Cu with 75% Au, i.e. 12.5% of each. Lines drawn parallel through X to the composition axes of the binary systems, i.e. the sides of the triangle, will meet the sides at 12.5% Ag, 12.5% Cu and 75% Au. Similarly, if we want to pinpoint an 18 ct alloy containing 5% Ag and 20% Cu, lines are drawn parallel to the sides up from the 20% Cu and 5% Ag point to meet at Y which obviously also meets the line drawn from 75% Au. The same arguments can be applied for all other ternary Au-Ag-Cu alloys. For convenience, the caratage lines for 22 ct, 14 ct and 9 ct are drawn at the 91.6%, 58.5% and 37.5% Au compositions, accordingly.

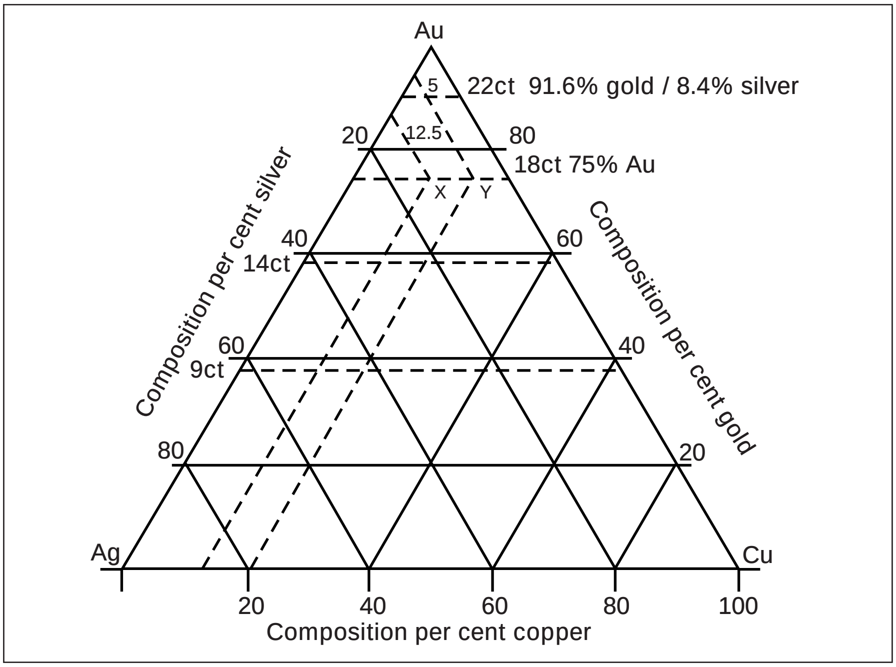

Figure 23 – Horizontal base for the Au-Ag-Cu ternary equilibrium diagram

The gold-silver-copper (Au-Ag-Cu) ternary diagram

The temperature axis is drawn vertically from the composition base and this means that the diagram cannot be a two-dimensional representation. Instead, it is three-dimensional and shaped like a prism, Figure 24. The binary phase diagrams for Au-Ag, Au-Cu and Ag-Cu form the sides of the prism and any binary alloy will have a composition somewhere on one of these three sides. The binary diagram for Au-Cu has been simplified slightly with respect to AuCu and AuCu$_3$ for ease of viewing. The alloying behaviour of any ternary alloy will be represented by considering the vertical line through the prism from its point on the composition base.

The effect of some of the features seen earlier in the binary diagrams can now be discussed. Instead of a liquidus line, there is a **liquidus surface**. It is possible to display this as a temperature contour map superimposed on the composition base, Figure 25. The influence of the binary Ag-Cu eutectic on the liquidus surface can be seen clearly as a valley extending into the triangle. The two-phase alpha plus beta ($\alpha + \beta$) field in the same binary system extends into the prism to produce a miscibility gap bounded by the dashed lines. The lower the temperature, the greater is this extension of the two-phase field into the prism. This can be demonstrated conveniently by taking a series of horizontal slices at different temperatures, known as **isothermal sections**, and superimposing them on the same diagram, Figure 26. It can now be seen that all 22 ct alloys will always be single-phase α solid solutions. The miscibility gap only just clips the 18 ct composition line at temperatures below 350°C whereas 14, 10 and 9 ct alloys are two-phase below 600-700°C except at compositions close to the Ag-rich and Cu-rich sides of the triangle.

The convention used earlier for labelling a miscibility gap in the gold-nickel (Au-Ni) system is used here. On crossing from the single-phase α field into the two-phase field as the temperature is lowered, the α-phase separates into α_1, the Au-Ag-rich phase, and α_2, the Au-Cu-rich phase. Take care, as some published

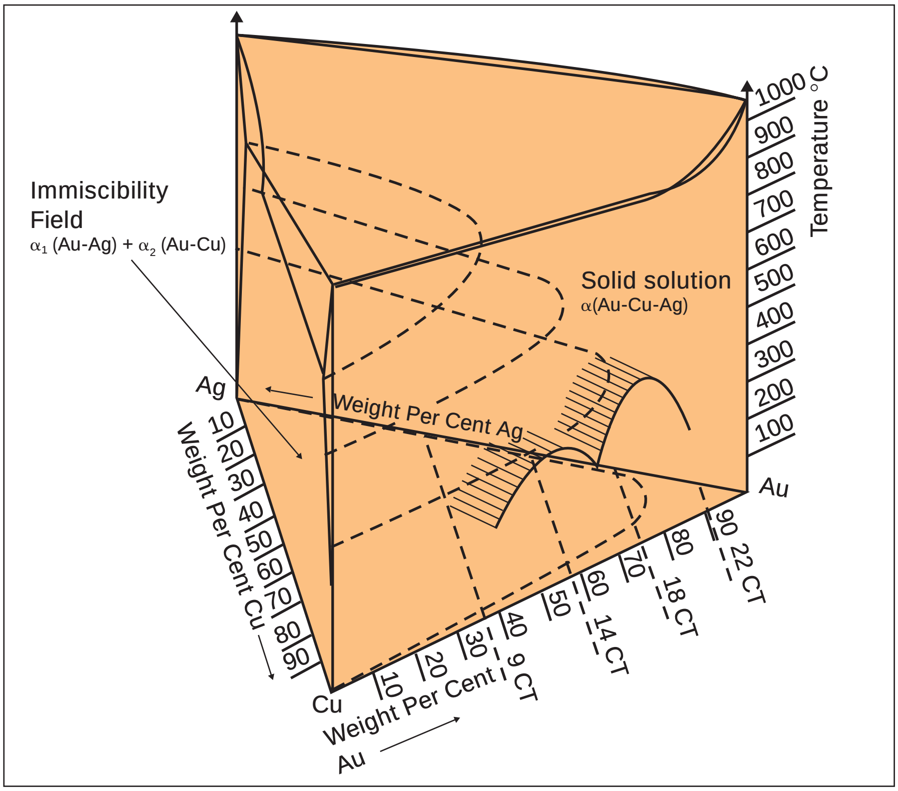

Figure 24 – Ternary phase diagram for Au-Ag-Cu alloys

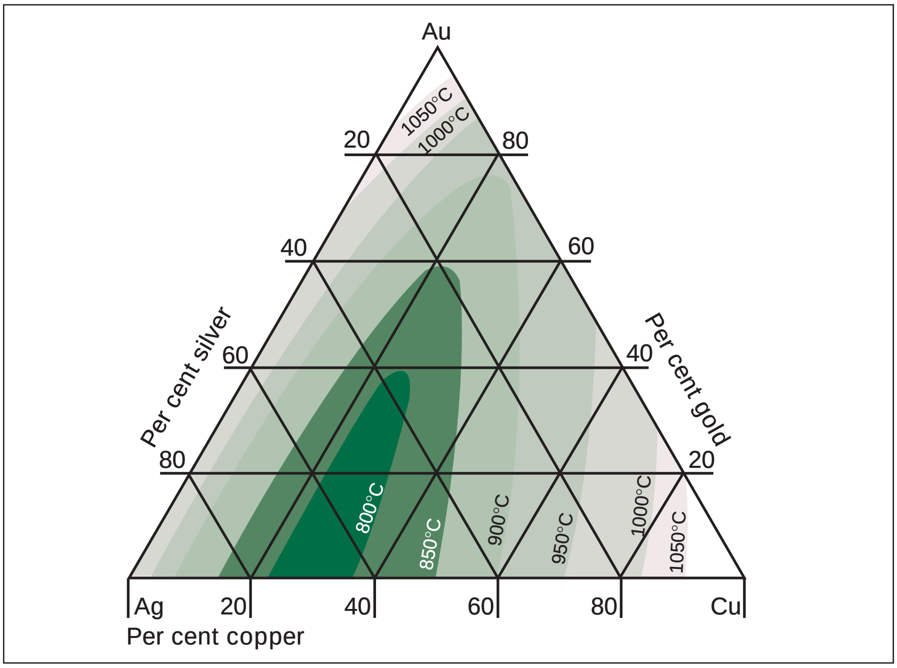

Figure 25 – The triangle can be used to show liquidus temperatures of the Au-Ag-Cu ternary system by means of temperature "controur" lines

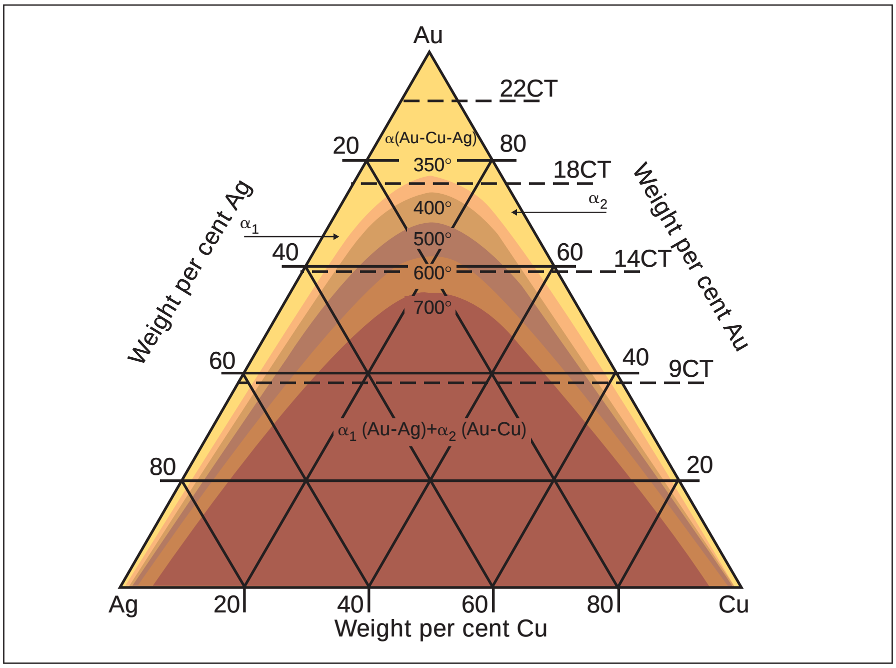

Figure 26 – Isothermal section projections showing extent of miscibility gap with temperature in the Au-Ag-Cu system

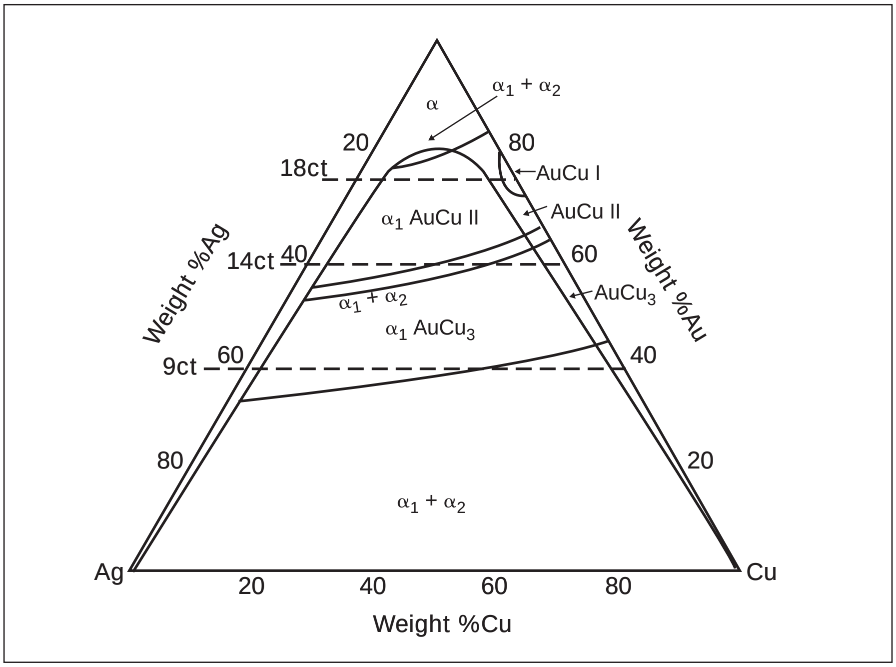

Figure 27 – Isothermal section at 300°C

diagrams reverse these numbers. These two separated phases are sometimes written as $\alpha_{Au\text{-}Ag}$ and $\alpha_{Au\text{-}Cu}$ to avoid confusion.

However, in actual fact, the miscibility gap is more complicated because the ordered phases, AuCu and $AuCu_3$, will also extend a little way into the prism from the side representing the binary Au-Cu system. This means that the α_2-phase may itself transform to AuCu II, AuCu I or $AuCu_3$, depending on composition. Figure 27 shows a slightly simplified version of the 300°C isotherm redrawn from data published by Susz *et al* and Yasuda (1,2). This has involved re-plotting the data in terms of composition in wt.% rather than at.%. It is acknowledged that there are slight discrepancies with the diagram published by Prince *et al* (3) but these do not affect the discussion presented here. Let us look at some examples of the equilibrium structures expected at this temperature. Silver-rich 18 ct greenish-yellow golds will be single-phase α-solid solution. As the copper content is increased at the expense of the copper, the alloys become two-phase α_1 + AuCu II and this will be the structure of a rich yellow 18 ct gold. Further copper increases will increase the amount of AuCu II and decrease the amount of α_1. Eventually, at high copper contents, the 18 ct red golds will be AuCu II + AuCu I or AuCu I. Similar arguments are applied for 14 ct alloys. The pale yellow Ag-rich 14 ct alloys are single phase α. From 5 to ~20%Cu the yellow alloys are two-phase α_1 AuCu II; from ~20 - 30% Cu the structures are $\alpha_1 + \alpha_2$; from ~30 - 37% Cu the structures of the red alloys are α_1 + $AuCu_3$; from ~37 - 41.5% Cu the alloys are single-phase $AuCu_3$. Strictly, three-phase fields separate the two-phase fields but they exist only over very small composition ranges (3). For the sake of simplicity, many authors ignore these details and refer only to $\alpha_1 + \alpha_2$ throughout the miscibility gap.

It is sometimes convenient to display vertical slices up through the prism from the 22, 18, 14, 10 and 9 ct composition lines on the base. These are referred to as **pseudo-binary sections**. The advantage is that the gold content is constant for each slice so that the composition depends on the Ag:Cu ratio. Provided this is

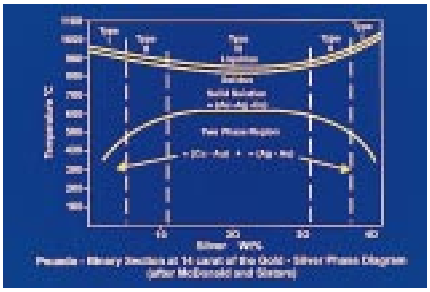

Figure 28a – Pseulo-binary section for 14 ct Au-Ag-Cu alloy

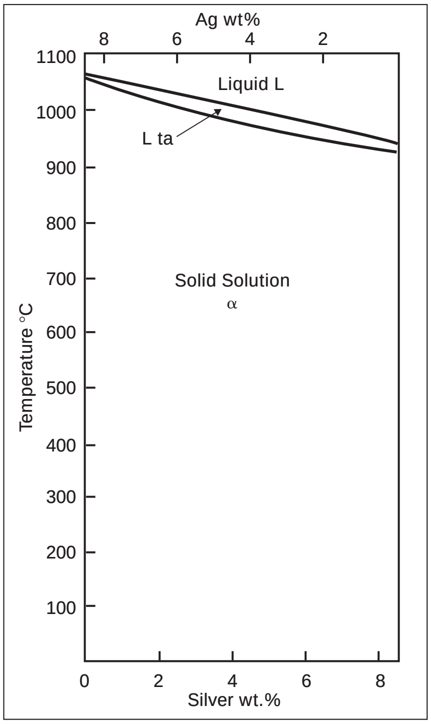

Figure 28b – Pseulo-binary section for 22 ct Au-Ag-Cu alloy

known, the sections can be used to describe the cooling behaviour as we saw earlier for binary diagrams. Examples are shown in Figure 28.

The colour triangle

Reference has already been made to the colours of the carat gold alloys. Figure 29 is the well-known Colour Triangle, which gives an indication of the colours to be expected for a ternary alloy of any composition. It must be remembered, however, that commercial coloured carat gold alloys may contain other elements, notably zinc, which may affect the colour and so this triangle must be used with caution.

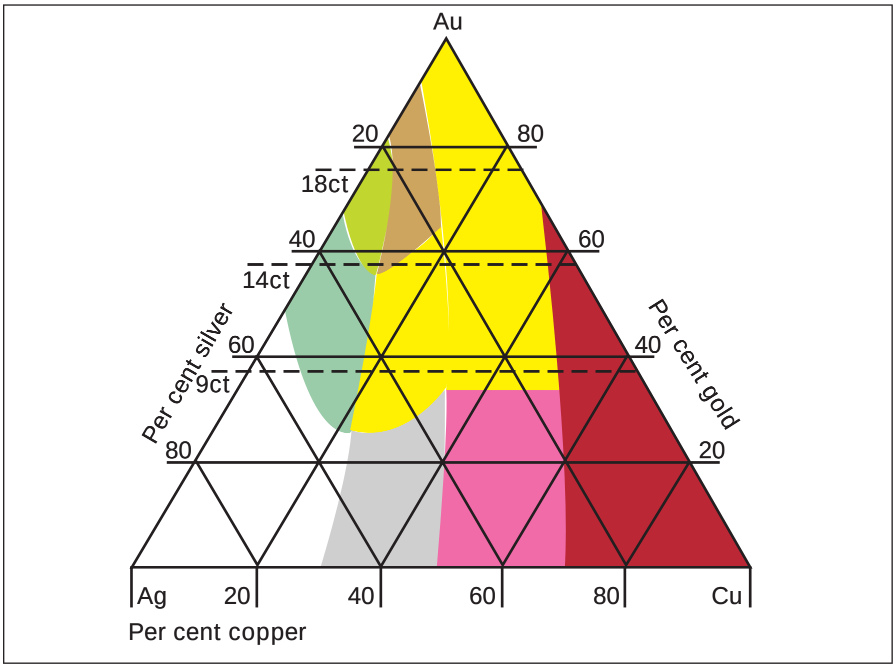

Figure 29 – The triangle again, this time being used to denote the different colours of alloys in Au-Ag-Cu systems

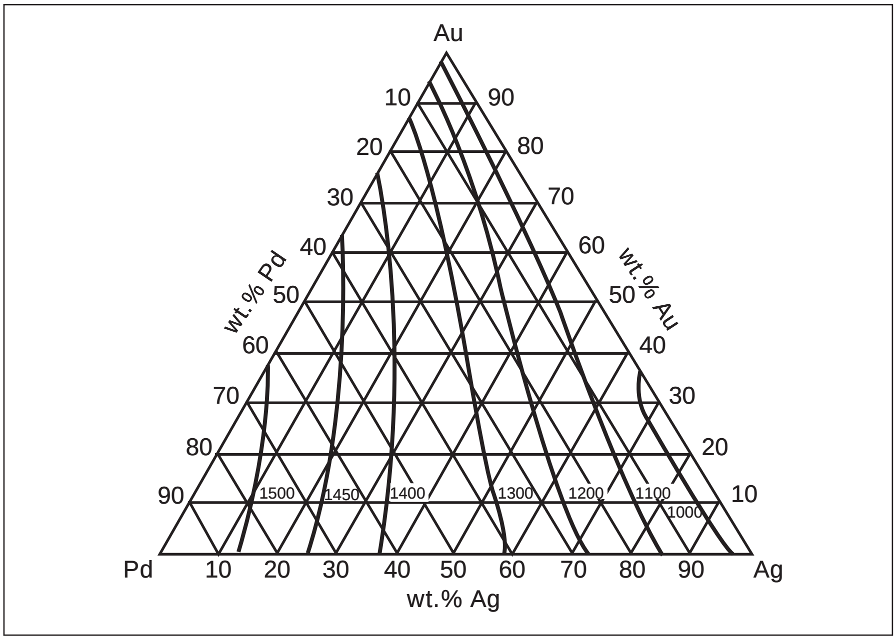

Figure 30 – The gold-silver-palladium ternary liquidus diagram illustrating a gradual transition of temperature with changing composition

Other important ternary alloy systems

a) Gold-silver-palladium

These three metals are completely soluble in each other and the diagram may be considered to show a single-phase solid solution at all compositions and temperatures below the solidus surface. Ordered phases have been reported in the gold-palladium (Au-Pd) binary system but the effect of silver additions have not been studied (3). Palladium raises the melting temperatures as shown in the liquidus surface contour plan for the ternary Au-Ag-Pd system, Figure 30. The ternary system is important because palladium is a whitening agent and a significant constituent of the palladium-white golds. Figure 31 (4) demonstrates the effect of composition on the colour of Au-Ag-Pd alloys.

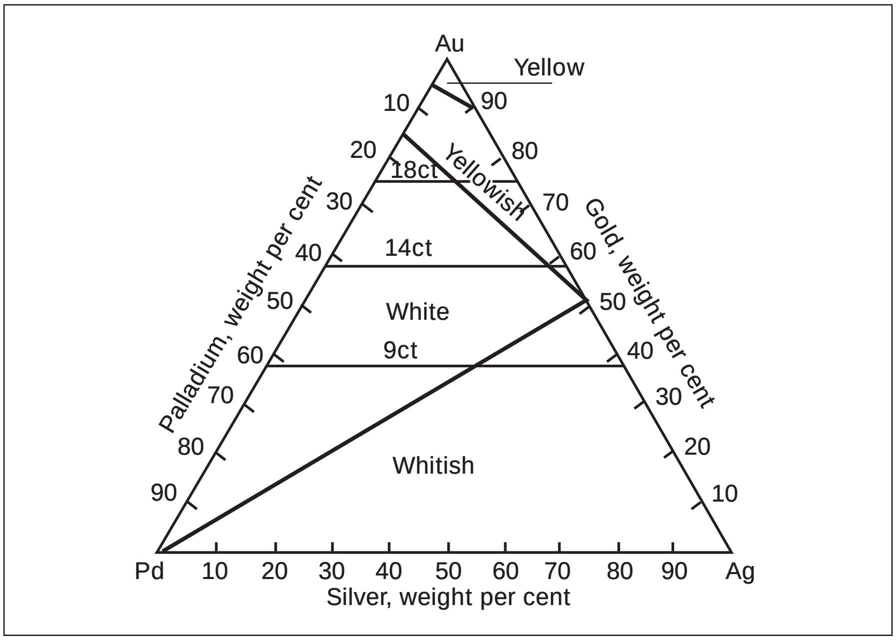

Figure 31 – The gold-silver-palladium ternary colour diagram indicatiing the range of whiteness as a function of composition

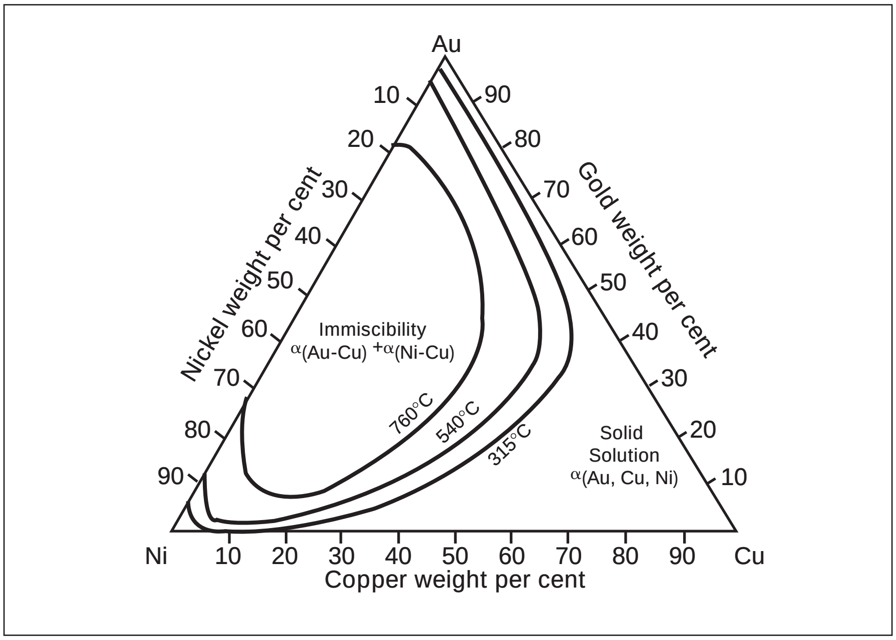

Figure 32 – Isothermal section projections showing the miscibility gap with temperature in the Au-Cu-Ni system

b) Gold-copper-nickel

Nickel is also a whitening agent and found in the nickel-white golds. The miscibility gap explored earlier in the gold-nickel (Au-Ni) binary system [see Part I, previous issue] extends into the ternary diagram for the Au-Cu-Ni system. This is seen in the isothermal section projections on the composition base in Figure 32 (5). It should be noted that the commercial nickel-white golds usually contain copper, silver and zinc, which will have an influence on the diagram as well as colour, workability and mechanical properties.

b) Additions of zinc

Zinc is often present in commercial coloured carat golds, particularly at the lower caratages. Strictly, one should consider the quaternary system gold-silver-copper-zinc (Au-Ag-Cu-Zn) but this then becomes a complicated issue. It is possible to make intelligent estimates on alloying behaviour by studying the relevant binary and ternary Au-Cu-Zn and Au-Ag-Zn diagrams (3).

Uses of phase diagrams

Phase diagrams have uses other than the prediction of solidification behaviour and subsequent phase transformations in the solid state, which we have looked at in some detail. Many properties of metals and alloys are very dependent on their microstructural condition. These include strength, hardness, ductility, workability, tarnishing, etc. Phase diagrams can be used to design alloys and heat treatments based on knowledge of phase transformations and ensuing microstructural changes. We shall briefly examine some of these aspects.

a) Solid solution strengthening

Pure metals do not always possess high strength and this is particularly true for gold, silver and platinum. One method for increasing strength is to cold work the metal and to rely on work hardening to give a higher strength, hardness and wear resistance. However, this will be at the expense of ductility and formability although, for some applications, this may be acceptable. Furthermore, any subsequent heating operations, such as in soldering, will anneal the metal in the heat-affected zone, thereby reducing the strength.

Alloying gives a much greater opportunity for influencing the mechanical properties. It has been mentioned that substituting solvent atoms with solute atoms will introduce strain into the parent metal crystal lattice and that this strain increases with increasing atomic size mismatch as well as increasing solute concentration. The effect of this increased lattice strain is to increase the strength and hardness without necessarily having any great deleterious effect on ductility. This is known as **solid solution strengthening**. It should come as no surprise to find that the greater the atomic size mismatch (i.e. the difference in atom diameters), the greater is the solid solution strengthening effect. It is well known that even in the softest annealed condition, copper additions to gold give greater strengthening than silver additions as shown in Tables 1 and 2.

The extent of solid solubility for any alloy system can be deduced from the phase diagram and that, coupled with a knowledge of atomic sizes, at least will give an indication of the degree of strengthening that may be achieved.

b) Strengthening by heat treatment

This has been discussed in some detail elsewhere (6) but it is worth repeating the essential features. We have seen that the coloured carat gold-silver-copper alloys are single-phase α at elevated temperatures below the solidus. Alloys having a caratage of 18 and lower may transform to $\alpha_1 + \alpha_2$ or to one of the ordered phases based on Au-Cu if they are slowly cooled, Figure 26. However, if they are quenched from the single-phase α field, this is retained as a supersaturated disordered solid solution and the phase transformations are suppressed. Treatment at temperature before quenching is referred to as **solution treatment**. Alloys in this condition will have maximum softness and ductility. Indeed, for this reason it is recommended that 14 and 18 ct alloys should always be water-quenched from 650°C and 550°C, respectively, if they are to receive further working. If the quenched alloys are given a low temperature ageing heat treatment, there is now a tendency to move towards the equilibrium condition. Very fine submicroscopic precipitation of the second phase may occur accompanied by a considerable increase in strength and hardness and reduction in ductility. Alternatively,

Table 1. Atomic radii

Metal	Atomic radius, nanometers (nm = 10^{-9}m)
Gold	0.1442
Silver	0.1443
Copper	0.1270

Note: The atomic radii depend on the type of bonding between atoms. In this case, for metals and alloys, the bonding is 'metallic bonding' and the above values apply.

Table 2. Strengthening effect of copper and silver in gold

	Hardness HV	Tensile Strength N mm^{-2}	Elongation %
Pure Gold	23	124	45
18ct 75% Au - 25% Ag. Annealed	32	185	36
18ct 75% Au - 25% Cu. Annealed	165	514	42

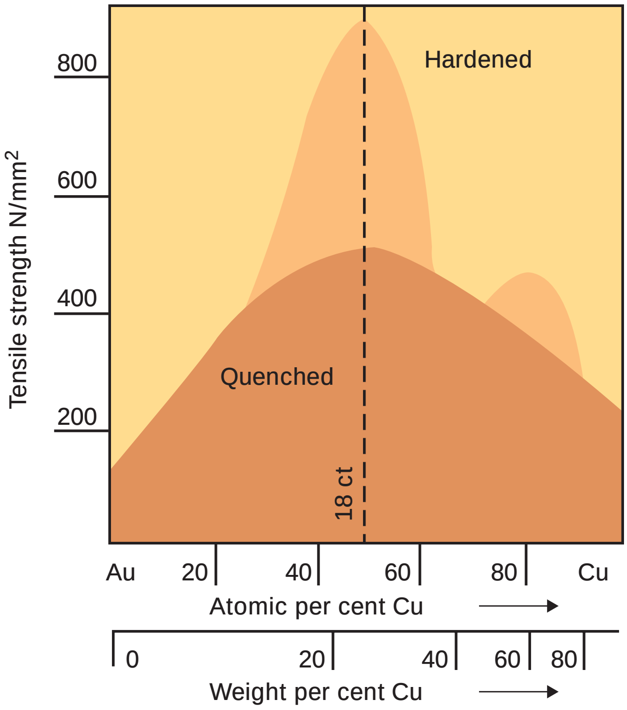

Figure 33 – Effect of heat treatment on the tensile strength of Au-Cu alloy

the disorder - to order transformation may occur and this, again, is accompanied by vast increases in strength and hardness, Figure 33. These treatments are called **age hardening** treatments. Figure 34 shows the effect of age hardening for all 14 ct ternary Au-Ag-Cu alloys. Alloy suppliers often recommend specific solution treatment and ageing temperatures and times.

The alloy which is known as 990 GOLD and which is gold – 1 wt.% titanium (Ti) is an age hardenable alloy (7). It can be seen from the phase diagram, Figure 15 [see Part I], that the alloy may be solution treated at 800°C, quenched and aged at 500°C to produce a fine precipitate of $TiAu_4$ in the gold-rich solid solution.

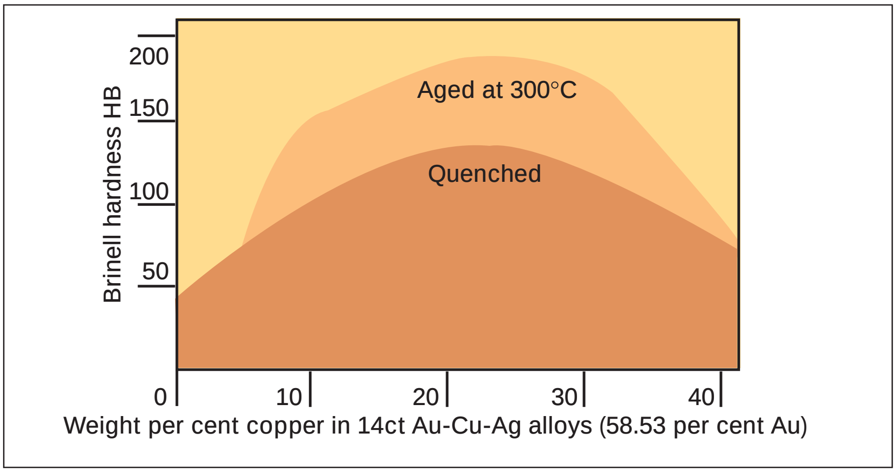

Figure 34 – Age harderning in 14 ct alloys

Table 3. Effect of zinc additions on the workability of 14 carat yellow gold alloys (5)

Gold, wt.%	Silver, wt.%	Copper, wt.%	Zinc, wt.%	Alloy Type
58.3	16.5	25.0	0.2	III
58.3	8.3	29.2	4.1	II
58.3	4.0	31.3	6.4	I

c) Microalloying

The development of 990 GOLD was done with the aim of marketing a high-carat gold with enhanced properties, particularly in South-East Asia and the Far East. In reality, its potential has been limited because it requires sophisticated processing techniques and its only main application has been in the watch industry. Nevertheless, considerable advances have been made in recent years in developing high-strength 24 carat golds (8,9). The 24 carat standard is defined as being a minimum of 990 fineness (99.0 wt.% Au) in some countries and a minimum of 995 fineness in others. This allows for microalloying additions in the range 0.1-0.5 wt.% and considerable improvements have been found for a number of materials. Much of the research work has entailed a study of phase diagrams to assist in alloy design.

d) Solder alloys

Solder alloys are required to have melting ranges below those of the parent metals or alloys being soldered. In addition, there may be other restrictions placed on them by hallmarking legislation. Eutectic alloys may fit the requirement because they often have the lowest melting temperatures in an alloy system. Reference has already been made to the classic case of the Pb-Sn tinman's solder. Silver solders are based around the Ag-Cu binary eutectic. Here, the eutectic temperature of 779°C is a little too high for successful use as a solder but additions of zinc and tin have the effect of lowering the eutectic temperature.

Similarly, gold solder alloys may be based on compositions around the valley in the liquidus surface of the ternary Au-Ag-Cu system, Figure 25. These alloys are known as '**self-type solders**'. These have limited use because of problems in trying to match the required caratage and colour with a suitable solidification range. Again, additions of other elements will reduce the solidification ranges. Traditionally, these have been zinc, cadmium, tin, and nickel. The use of cadmium is not recommended because of its toxicity. Fortunately, cadmium-free solders are commercially available (10-12). Some of these contain small additions of indium.

Recently, low melting point gold solder alloys have been developed based on the eutectic compositions in the gold-silicon (Au-Si) and gold-germanium (Au-Ge) binary systems with eutectic temperatures at 363 and 361°C, respectively (13). Furthermore, a eutectic valley exists across the liquidus surface in the ternary Au-Ge-Si joining these binary eutectics. There is a point along this valley that corresponds to a 22 ct gold composition at 91.6% Au-6.7% Ge-1.7% Si.

e) Workability

A final example makes use of the fact that single-phase alloys will have better ductility and workability than two-phase alloys. McDonald and Sistare (5) introduced the concept of three 'types' of alloy based on the miscibility gap in the Au-Ag-Cu system for 14 ct alloys, Figure 28. Type I alloys are based on the solid solutions either side of the gap. Alloys of this type are soft in the annealed condition and have good workability. Type II alloys are moderately soft but are just into the two-phase field $\alpha_1 + \alpha_2$. They are age hardenable. Type III alloys across the centre of the gap are hard in the annealed condition and are difficult to quench. They have poor workability.

Additions of zinc have the effect of lowering the temperatures of the boundary between the single-phase and two-phase fields and reducing the width of the miscibility gap. This has the effect of increasing the extent of Types I and II alloys and improving the range of alloys with good workability whilst retaining a desired colour. This is the reason why the wrought low-carat gold alloys, e.g. for sheet, wire, tube and chain, contain zinc, Table 3.

This was vividly brought home to the author when, as the result of a seminar given in Istanbul, Turkey, a manufacturer, who had been experiencing cracking problems in the production of 14 carat yellow gold chain, made an alloy with a higher zinc content and immediately solved the problem.

Workability will be deleteriously affected if the alloy contains embrittling impurities or hard spots. One well-known example is that the presence of small amounts (< 0.1 %) of lead will cause catastrophic embrittlement in gold (14). The phase diagram shows that this is due to a low melting point phase Au_2Pb, which forms in the grain boundaries.

Concluding remarks

It is hoped that this paper has demonstrated that a comprehension of phase diagrams is not too difficult. Considerable benefits are to be gained by jewellers and manufacturers if they can follow solidification and phase transformation behaviour, thereby increasing their understanding of the alloys they are using. It is of assistance in alloy selection in terms of the requirements of the product, e.g. chain or castings, mechanical properties, workability, service requirements, caratage, colour, etc. There are also benefits with regard to defect analysis, quality assurance and quality control.

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