

A Plain Man's Guide To Alloy Phase Diagrams: Their Use In Jewellery Manufacture - Part 1

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Introduction

Manufacturers who produce jewellery by mass production techniques, as well as those skilled at making jewellery as a craft, hopefully will be aware that in recent years there have been many publications concerned with the metals and alloys used for making jewellery and decorative metalware. One only has to look at the many issues of *Gold Technology*, for example. Naturally, the main interest lies in selecting the best metal or alloy for the task in hand and involves considerations of such factors as castability, strength and hardness, workability, colour, caratage, and so on. It may not always be appreciated that these depend on alloying behaviour, alloy composition and microstructural condition within the alloy. Fortunately, metallurgists and chemists have developed a method, which goes a long way to understanding and explaining these characteristics. This is by describing alloying behaviour using **phase diagrams**.

Phase diagrams are analogous to road maps in that provided you know the composition of the alloy you are

dealing with and the temperature, say, room temperature or any furnace temperature, then you can pinpoint exactly where you are on the 'map'. Furthermore, the 'map' shows what structural changes may occur in the alloy as you navigate from one temperature to another. In essence, phase diagrams may be used to predict structure and properties and what opportunities exist for manipulating the properties of strength, hardness and ductility or formability.

It is the purpose of this paper to attempt to describe and explain these diagrams so that they may be understood and interpreted with benefit to all who make jewellery. There is a tendency to think that they are complicated and are the preserve of the scientist and technologist but yet many of the diagrams connected with the carat gold alloys and those of other precious metals are relatively simple once a basic knowledge of the underlying principles are understood.

Definitions

Before looking at the construction of phase diagrams, it is necessary to

define some of the terms that will be used.

A question often asked is "What is meant by the word '**phase**'?" A phase is a substance that is chemically and structurally homogeneous within itself but is physically separated by definite boundary surfaces from other substances or phases and is different from them in composition, physical state or crystal structure.

For example, it is well known that matter can exist in three forms, Figure 1. One only has to think of steam, water and ice. At high temperatures above the boiling point for any substance, it will be a gas or vapour where the atoms or molecules are spaced apart and there is no structural relationship between them. As the temperature falls below the boiling point, the vapour condenses to a liquid where the atoms are closer together and there is a rudimentary structure with the atoms forming clusters. These clusters are not stable and they continually break up and reform. As the temperature falls still further, the freezing (melting) point is reached and the liquid solidifies. A few of the

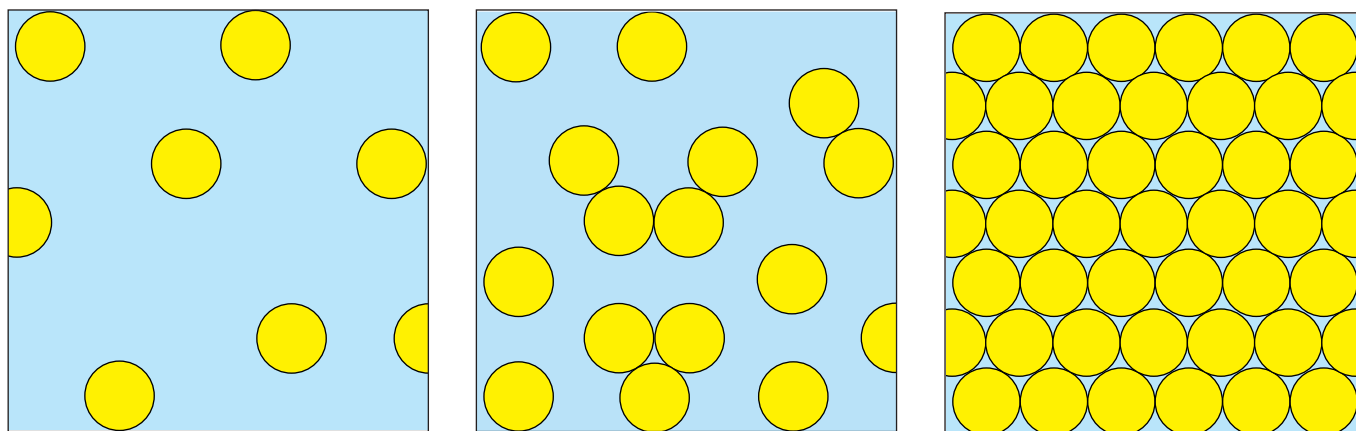


Figure 1 - Atomic arrangement in
(a) gases

(b) liquids

(c) solids

clusters grow and attain a critical size where instead of breaking up they become stable and continue to grow to form solid crystals having a regular geometrical arrangement of atoms in a lattice. This is the process of nucleation and growth, a necessary step in the solidification of metals and alloys during casting. This has been described in more detail elsewhere (1,2).

It can be seen, therefore, that pure metals can exist as a vapour phase, a liquid phase or a solid phase depending on temperature. In this case, the chemical composition of each phase is the same, i.e. that of the pure metal, but the physical state is different, as is the structural condition within each phase. Alloys can exist also in the vapour, liquid and solid states but there is an added variable, namely, the composition of the alloy. This means that alloys may exist with more than one liquid phase or solid phase. We need not concern ourselves with alloys having two or more liquid phases because they are relatively rare and not relevant to jewellery alloys. In the solid state in, say, a two-phase alloy, the composition and crystal structure within each phase will be uniform but different to those of the other phase. Furthermore, one will need to consider how many constituents or components are present in the alloy. This affects the number of phases that may be present in the alloy at a particular temperature.

The **number of components** is the smallest number of substances that must be listed to describe completely the chemical composition of the system being considered. In alloy systems, this is usually the number of chemical elements present. For example, gold-silver (Au-Ag) alloys are referred to as binary alloys because only two components, namely, gold and silver are present, whereas gold-silver-copper (Au-Ag-Cu) is a ternary alloy system with three components, the Au-Ag-Cu-Zn (zinc) system gives quaternary alloys, etc. Binary alloys may have one or two phases depending on composition and temperature; ternary alloys may have up to three phases.

The variables of temperature and composition are sometimes referred to as **degrees of freedom**. Strictly, pressure is also a variable. Since almost all metallurgical processing such as alloying, casting, heat treatment, etc. is done at atmospheric pressure, which is virtually constant and, also, as it requires very great changes in pressure to affect phase changes, pressure can be ignored as a variable for practical purposes.

Phase mixtures are where two or more phases co-exist in equilibrium. A suitable analogy, which is easily understood, is a mixture of oil and water. Here we have two liquid phases that are insoluble in each other. The physical state is the same in that they are both liquids. Within

each liquid phase, the composition and structure are the same, i.e. homogeneous, but each phase is different from the other and there is a definite boundary between the phases. This analogy enables us to glimpse what is meant by **microstructural** condition, Figure 2. In one case, the oil and water are co-existing with the oil phase floating on top of the water phase, simply because it has a lower density. If the container is rapidly shaken, the agitation causes the oil and water to break up into droplets that become dispersed in each other to form an emulsion. However, this is still a two-phase mixture with definite boundaries between each type of liquid phase but the microstructural condition has changed.

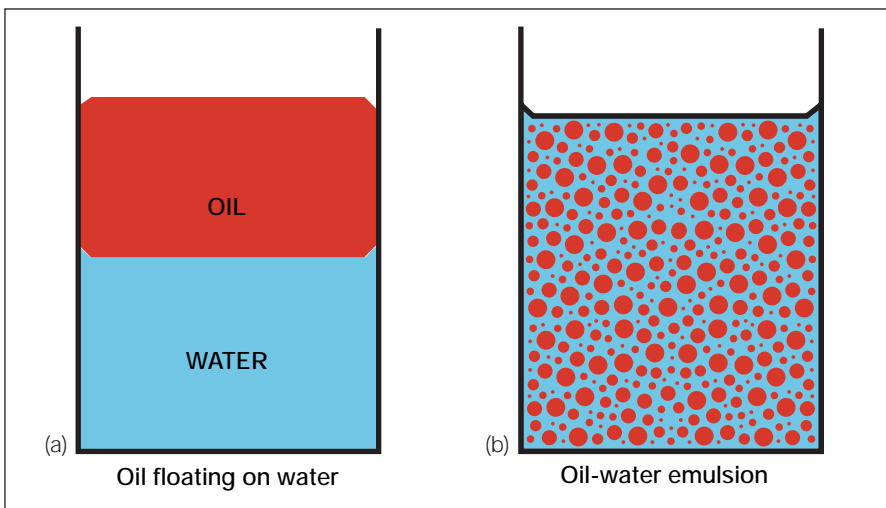


Figure 2 - Two phases co-existing in equilibrium (a) oil floating on water (b) oil-water emulsion. Both have the same phases but (a) has a different microstructure to (b)

Solutions are substances where one component has dissolved in another to give a single phase. Staying with a liquid analogy, water and alcohol will mix completely in each other to produce a single liquid phase that is structurally and chemically homogeneous within itself. The chemical composition of that phase will be determined by the relative amounts of water and alcohol used to make the solution. Similarly, salt can be dissolved in water to give a single phase salt solution, although in this case there is a limit to the amount of salt that can be dissolved in a given amount of water at a given temperature, i.e. a **limit of solubility**. In metallic alloy systems, not only can we have liquid alloy solutions but also below the melting range, the solution may be retained as a **solid solution**. Figure 3 shows a two-dimensional representation of a single phase solid solution where one metal (**the solute**) has 'dissolved' in another (**the solvent**) by substituting some of the parent solvent metal atoms with solute metal atoms in the crystal lattice of the parent metal. This is known as a **substitutional solid solution**¹. It is single phase in that the crystal lattice structure and the alloy composition are the same

throughout the phase. We shall see later that there may be a **limit of solid solubility** in solid alloy phases for a given temperature.

Intermediate phases are solid alloy phases that may exist in some, but not all, alloy systems. As the name suggests, they have composition ranges which are intermediate

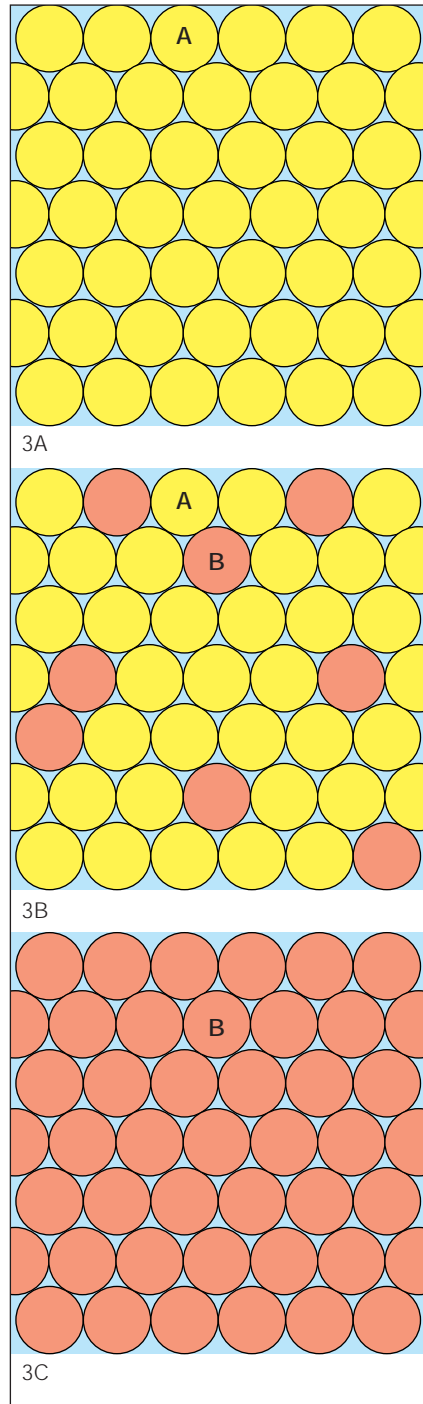


Figure 3 - Formation of a complete series of solid solutions between 2 metals, e.g. gold ● and silver ● (or copper above 410°C)

between and do not include the pure parent metals and which have a crystal structure different to that of either of the parent metals. A particular type of intermediate phase is an **intermetallic compound**. Intermediate solid solutions may exist over a wide composition range whereas intermetallic compounds exist either over a very narrow composition range or at a fixed composition based on a simple ratio of the parent metal atoms. For example, in the Au-Cu binary system there are two intermetallic compounds, AuCu and AuCu₃, which means that they have atomic ratios of one atom of gold to one of copper and one atom of gold to three of copper, respectively. To take this a stage further, these ratios can be expressed as a composition in terms of atomic percentage. A ratio of Au:Cu of 1:1 means that the alloy or compound has a composition of 50 atomic % Au and 50 atomic % Cu, usually abbreviated to 50 at.%. Similarly the 1:3 ratio gives 25 at.% Au and 75 at.% Cu.

We have just seen that **alloy composition** may be expressed in terms of atomic percentage, which is very useful when seeking explanations for certain types of metallurgical behaviour but which is not helpful when making alloys by weighing out the required proportions as so many grams of each constituent. Consequently, composition is often expressed more conveniently in terms of weight percentage (wt.%). Therefore, phase diagrams may be plotted either in terms of at.% or wt.% composition. The atomic percentage is not the same as the weight percentage because the atomic weights of each constituent metal are different. There is a simple formula for converting atomic % to weight % for binary alloy systems.

$$W = \frac{XM}{XM + (100-X)N} \times 100$$

where W = wt.% of metal A
X = at.% of metal A
M = atomic weight of metal A
N = atomic weight of metal B

¹ If there is a great difference in size between the solvent and solute metal atoms, then the smaller solute atoms can sit in the interstices, or spaces, between the solvent metal atoms in its lattice. This is known as an interstitial solid solution. The classic example is carbon atoms in iron to form steel.

If we take the 1:1 ratio for AuCu at 50 at.% Au and apply the formula knowing that the atomic weight of gold is 196.97 and that of copper is 63.55, then it can be seen that this composition works out at virtually 75 wt.% Au - 25 wt.% Cu. This is the composition for an 18 carat red gold alloy. Similarly, the 1:3 ratio (25at.% Au) is equivalent to 50.8 wt.% Au - 49.2 wt.% Cu which is approximately at 12 carat. These intermetallic compounds have an important influence on the characteristics of the coloured carat gold alloys, as we shall see later.

Finally, phase diagrams are often referred to as **phase equilibrium diagrams** or simply equilibrium diagrams. All systems tend to move to an equilibrium condition when all possible reactions are complete and there is no further change, provided there are no further changes to temperature or composition. Consider the simple case of an ice cube in a freezer compartment at, say, -10°C. If it is taken out and placed in air at 25°C, the cube is no longer at equilibrium. It will melt to form a puddle of water and eventually the water will attain a uniform temperature of 25°C, i.e. it will have reached the equilibrium condition. Obviously, it takes time to reach equilibrium. Phase diagrams are usually plotted assuming that equilibrium conditions have been reached for any given temperature and composition. In practice, particularly when casting, non-

equilibrium conditions may exist and care must be taken in interpreting phase diagrams. This limitation will be reviewed in more detail later.

Cooling curves and their interpretation

The construction of phase diagrams is best explained by considering the data supplied by a **cooling curve**. This is a plot of temperature versus time when a metal or alloy is cooled from the melt. Figure 4 shows typical curves obtained when the drop in temperature with time is measured after the heat source has been removed from a crucible containing the metal or alloy being examined.

Figure 4a is the type of curve displayed by a pure metal. The temperature of the melt falls with increasing time, measured say in seconds, until point S is reached. The temperature then remains constant to point F after which it falls further as the solid continues to cool. Solidification from the liquid phase to the solid phase occurs along the plateau, with the start of solidification at S and the completion at F. The reason for the plateau is that heat is given out when liquid transforms to a solid, known as the latent heat of solidification, which counteracts the tendency for the temperature to fall in the absence of an external heat source. This constant temperature plateau is the characteristic freezing - or solidification - temperature for a pure metal. Conversely, if the solid is heated to cause melting, the curve is

reversed and this temperature is also the melting point. In practice, a slight decrease in temperature below S may be observed before it climbs back to the plateau. This is known as 'undercooling' and is due to the requirement of forming crystal nuclei from which solidification proceeds. It need not concern us further.

Figure 4b is the type of curve obtained when an alloy melt solidifies to form a single-phase solid solution. Again solidification starts at S and is complete at F but it will be noticed that, instead of a characteristic fixed solidification or melting point, solidification occurs over a range of temperature. Between S and F, two phases, namely, the liquid phase and the solidifying solid solution are co-existing in equilibrium. The point S is marked by a change in slope (an 'arrest') in the curve and point F by a further change.

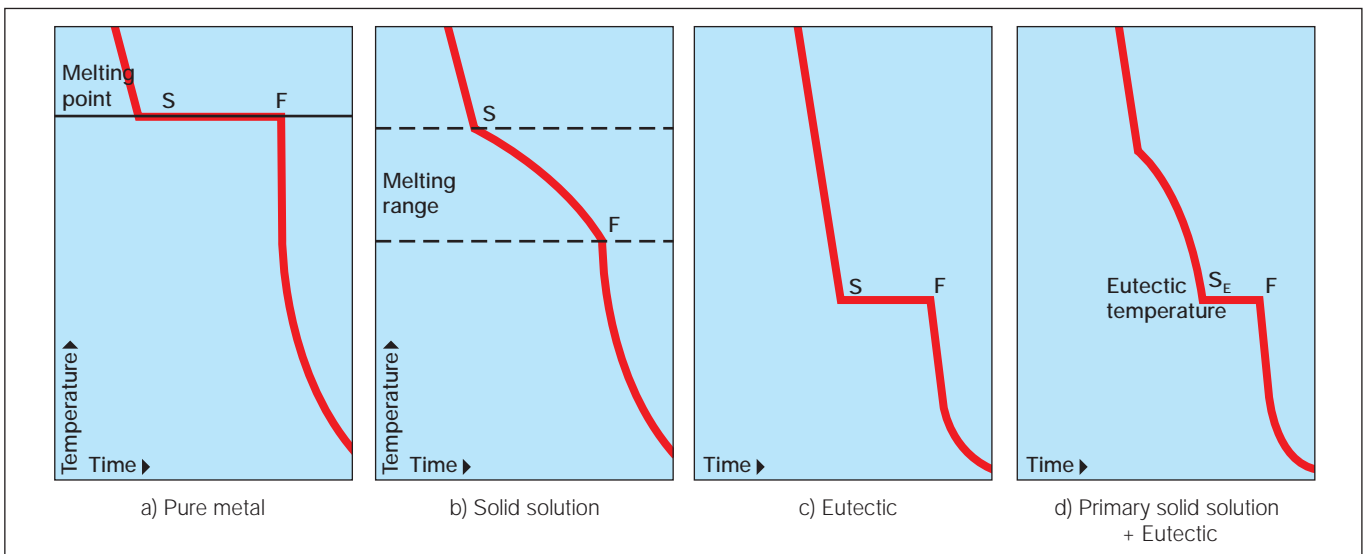


Figure 4 - Cooling curves of pure metals and alloys

The curve in Figure 4c appears, at first sight, to be a pure metal because there is a plateau and the solidification temperature is constant. However, this behaviour can be displayed by certain alloys of fixed compositions and where the solidification temperature is below those of the parent metals from which the alloy is composed. These are known as **eutectic alloys** where a single-phase liquid solidifies to two or more solid phases, as will be described later. The temperature of solidification (or melting) is the **eutectic temperature**. (Note: There are occasional examples of fixed composition alloys having a cooling curve of type 4c which are not eutectics since liquid solidifies to single phase solution, e.g. the binary alloy 80 wt.%Au-20 wt.%Cu). A good example familiar to all is the eutectic alloy of 63 wt.% tin-37 wt.% lead. Pure lead and pure tin solidify at 327°C and 232°C, respectively, whereas the eutectic temperature is

183°C. This alloy is known as *tinmans' solder* or *radio solder* because it is a solder alloy which melts and solidifies rapidly, a desirable property when making solder joints for electrical connections. Many commercially important solder and brazing alloys are based around eutectic alloy compositions. One very important eutectic reaction is to be found in the Ag-Cu binary system at 28.1 wt.% Cu and a eutectic temperature at 779°C. This has a significant effect not only on the binary phase diagram but also the ternary Au-Ag-Cu system and the alloying behaviour of the coloured carat golds. Figure 4d indicates that solidification starts at S with the formation of a solid solution phase because the temperature continues to fall as solidification proceeds. However, at point S_E, the remaining liquid solidifies via a eutectic reaction and this is complete at point F. *Plumber's solder* of composition 70 wt.% lead (Pb) - 30 wt.% tin (Sn) is an

example of an alloy having this type of cooling curve. The presence of a solidification range allows the plumber to 'wipe' a joint while the solder has a pasty consistency.

Construction of phase diagrams

A good example to show how cooling curve data are used to construct a phase diagram is the gold - silver (Au-Ag) binary alloy system, Figure 5. The start (S) and completion (F) temperatures of solidification are measured on cooling curves for a series of alloys ranging from pure gold across to pure silver. These are then plotted on a diagram with temperature in, say, degrees Celsius (°C) as the vertical axis and alloy composition in terms of one of the parent constituent metals from 0 to 100%, either as wt.% or at.%, as the horizontal axis. It can be seen that a line is drawn connecting the S points from pure gold at 1064°C to pure silver at 962°C. This line denotes the temperature at which solidification starts for any alloy in the system and is known as the **liquidus**. Similarly, the line drawn connecting the F points represents the completion of solidification for any alloy and is known as the **solidus**. It will be noted that the lines converge for the pure metals which is not surprising since we have established that here, solidification occurs at characteristic fixed temperatures for gold and silver (and all pure metals).

The area of the diagram above the liquidus is the liquid phase field and, by convention, is labelled L. It is a single phase because gold and silver will readily form a liquid metal solution at all compositions. There are a very few cases where liquid metals are insoluble (**immiscible**) in each other but they need not concern those working with precious metal alloys or even the vast majority of base-metal alloy systems. Below the solidus, any alloy in the system has formed a single solid solution phase. Because the gold atoms in its crystal lattice can be replaced or substituted by silver atoms at all compositions from 0 to 100%, we say that there is a **complete series of solid solutions**. Again, by convention, solid phase fields are denoted using letters of the Greek alphabet and this is the **alpha (α) phase field**. The area

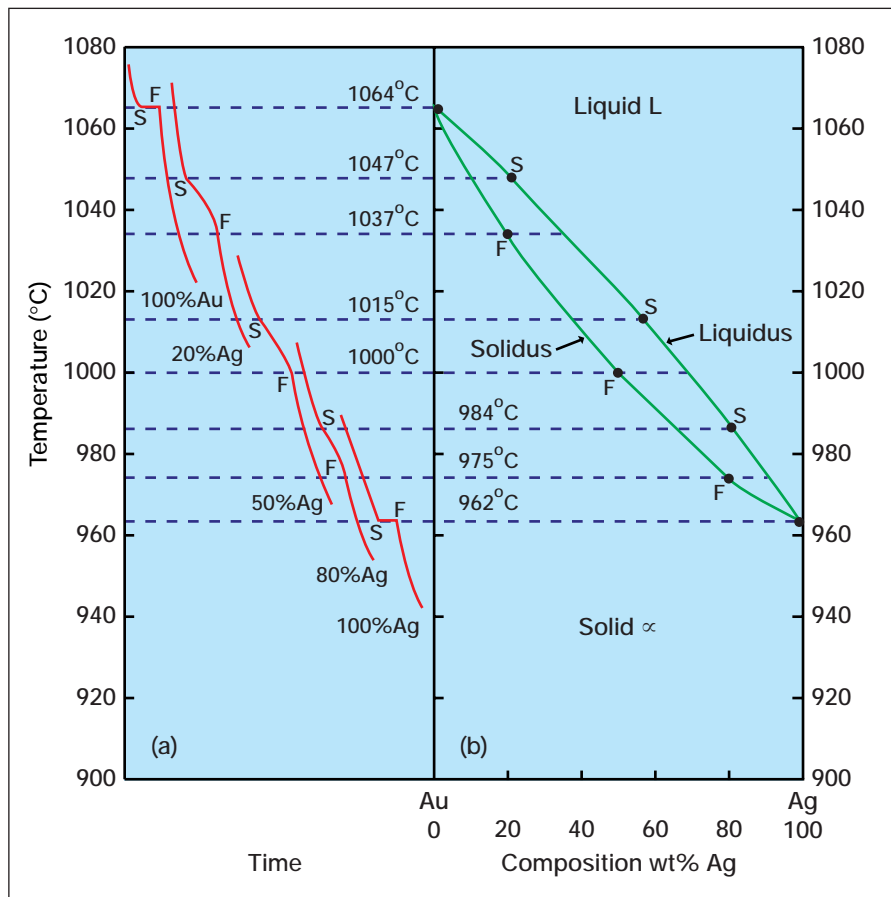


Figure 5 - Construction of the binary gold-silver phase diagram from cooling curves (a) cooling curves (b) phase diagram

between the liquidus and the solidus denotes the solidification temperature range for the various alloys. It is a **two-phase field** because liquid L and solid α co-exist in equilibrium as the alloys solidify. It is labelled 'L + α ' to indicate the two phases present. There are no further phase changes in the Au-Ag binary system as the alloys continue to cool to room temperature. Incidentally, phase diagrams in metallic systems do not extend up into the vapour phase as the temperatures are very high and there is little metallurgical interest.

Let us now look at the construction of a diagram containing a eutectic reaction. A good example is the silver

- copper (Ag-Cu) binary system. The melting points (solidification points) for silver and copper are 962°C and 1083°C, respectively. Consider the cooling curves for the pure metals and five Ag-Cu alloys having compositions of 5, 15, 28.1, 50 and 95 wt.% Cu, Figure 6. Plotting the S and F points on the temperature versus composition diagram, joining the lines and extrapolating between points gives a plot as shown in Figure 7. Obviously, it is not complete and one would have to plot cooling curves for many more compositions to establish the ends of the horizontal temperature line. In fact, they are at 8.8 and 92 wt.% Cu, respectively.

The horizontal temperature line at 779°C is the eutectic temperature, i.e. the temperature at which the eutectic reaction takes place. The eutectic composition is at 71.9 wt.% Ag - 28.1 wt.% Cu. Liquid alloy at this composition will solidify to produce an intimate mixture of two solid phases (L \rightarrow α + β). You may ask, "Where are the two phases in the diagram?" Careful examination of the cooling curves for the 5 and 95% alloys may show further arrests, i.e. slope changes, at temperatures below F, say at M and N, Figure 6. This implies that the single-phase solid solutions formed after solidification are undergoing phase transformations in the solid state at lower temperatures. The change in slope is due to the fact that heat is evolved during the phase change, the **latent heat of transformation**.

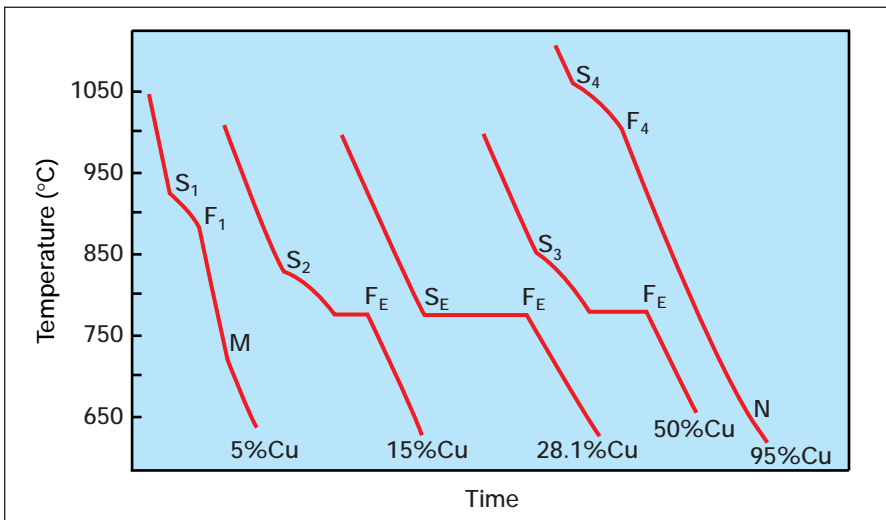


Figure 6 - Cooling curves for silver-copper alloys

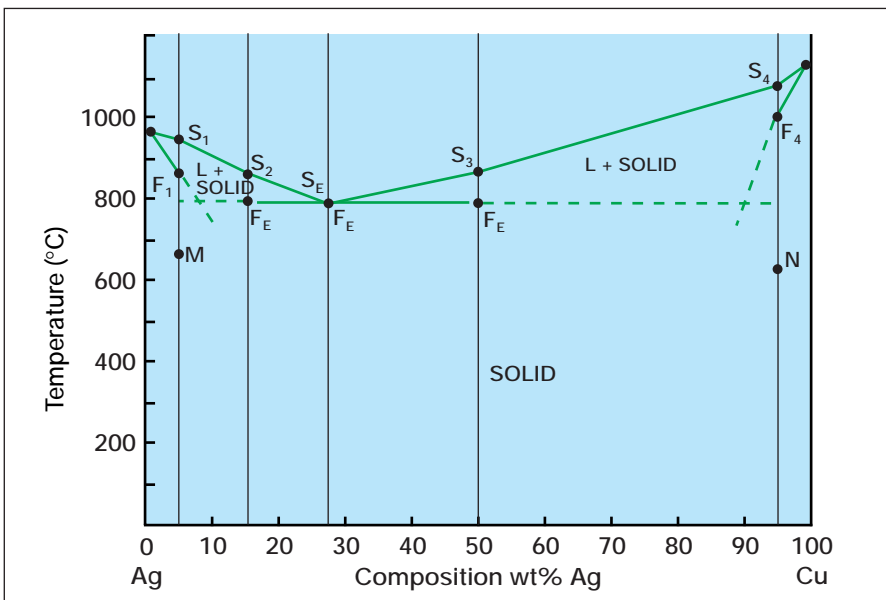


Figure 7 - Part construction of the silver-copper phase diagram

The completed phase diagram is shown in Figure 8. The liquidus line is the upper line AED, above which there is the liquid phase field L. The solidus is ABCE. The line ABF defines the limit of the alpha phase field (labelled α) which is the solid solution of copper atoms dissolved in the silver lattice. In other words, it is not possible to get a complete series of solid solutions in this alloy system. The limit of partial solid solubility falls with decreasing temperature and is negligible at room temperature. Similarly, there is a limit to the amount of silver that can be dissolved in the copper lattice. This limit is defined by the line DCG and the single-phase solid solution based on the copper lattice is the beta (β) phase. The area below the horizontal eutectic temperature line bounded by FBECG is a two-phase field containing a mixture of the two phases from each side, namely, $\alpha + \beta$. This illustrates an important rule for binary phase diagrams in that single-phase fields are always separated by two-phase fields.

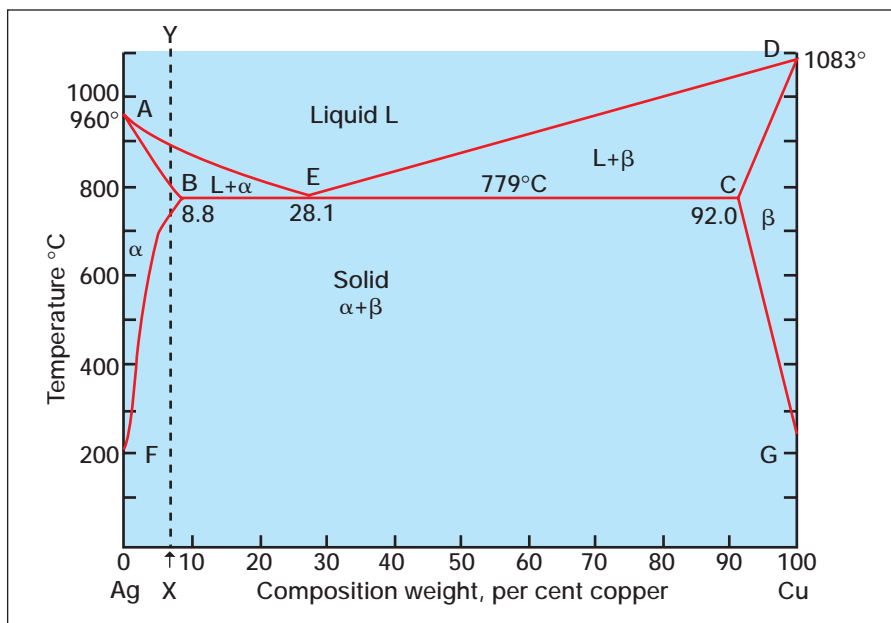


Figure 8 - Phase diagram for the silver-copper system

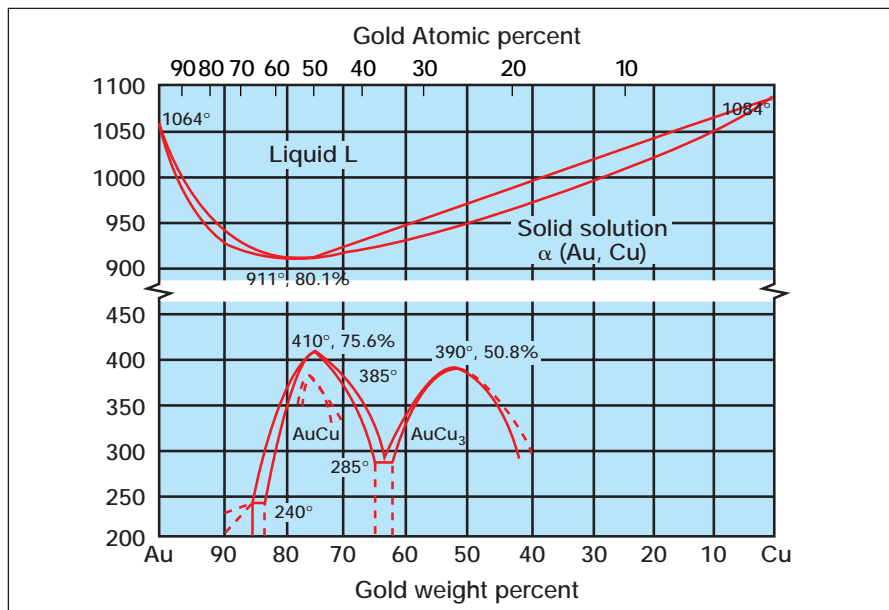


Figure 9 - Gold-copper binary phase diagram

Another binary alloy phase diagram of considerable importance to the jewellery manufacturer is that for the gold - copper (Au-Cu) system, Figure 9. Again, the upper line is the liquidus above, which there is the liquid phase L. The lower line is the solidus below which all alloys are solid. In this case, all alloys solidify to give a complete series of solid solutions, just as was seen in the Au-Ag system, and the α -phase field extends from 0 to 100% Cu. The two-phase field, L + α exists between the

liquidus and the solidus. As mentioned earlier, the liquidus and solidus lines coincide at a specific composition (80 wt.% Au) and temperature (911°C), but this is not a eutectic, since the liquid transforms to a single solid α -phase and not to two solid phases. Unlike the Au-Ag system, the α -phase is not stable at all temperatures and compositions down to room temperature. Further phase changes occur in certain composition ranges below certain temperatures. Alloys centred around 50 at.% (75.6 wt.%) Au transform at 410°C to the intermediate phase AuCu II (based on the intermetallic compound AuCu) and this in turn undergoes another transformation to AuCu I at a slightly lower temperature, Figure 9. Alloys centred on the composition 25 at.% (50.8 wt.%) Au transform at 390°C to the intermetallic AuCu₃. These transformations are of a special type known as disorder-order transformations and have a profound influence on the workability of carat gold alloys, particularly red golds.

One could continue to give other examples of binary phase diagrams where gold is one of the components and where other features may be noted. However, their construction will always follow the method shown in the above examples. It is not always easy to detect the arrests on simple cooling curves because the lengths of a plateau or the lines of

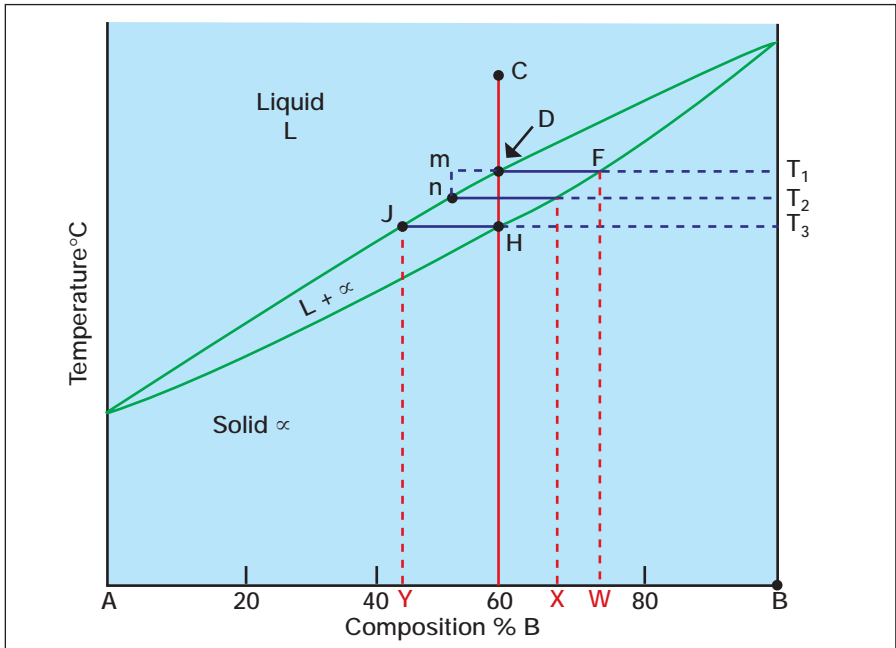


Figure 10 - Solidification of a solid solution under equilibrium conditions

Draw a vertical line up from this point on the composition axis to point C above the liquidus. At this temperature, the alloy is molten with a uniform composition. On cooling, solidification starts at D on the liquidus at temperature T_1 .

The first solid to form is not of composition 40% A - 60% B, as might have been expected. The composition of the first solid α is found by drawing a horizontal line, known as a **tie line**, across the two-phase 'L + α ' field to point F on the other phase boundary, in this case the solidus. Dropping a line to the axis gives a composition 'w' for the first solid to form. Since the overall composition must be unchanged at 40% A - 60% B, the remaining liquid must become enriched in Metal A to some imaginary point 'm'. This liquid has to cool to point 'n' at temperature T_2 before solidification can continue. This new solid forms on the first nuclei of composition 'w' and after allowing diffusion to even out the solid composition, the solid will now have the composition 'x'. As the temperature continues to fall, this process is repeated until the vertical alloy composition line crosses the solidus at H at temperature T_3 . The last drop of liquid to solidify has reached point J and attained a composition given by 'y'. Under very slow equilibrium cooling conditions, the solid α -phase has evened out its composition by diffusion and has now reached the overall composition of the alloy, namely, 40% A - 60% B. Another way to look at this sequence is to note that as the solid forms, it changes its composition by diffusion and increases in amount along the line $F \rightarrow H$. The remaining liquid changes its composition and decreases in amount along the line $D \rightarrow J$.

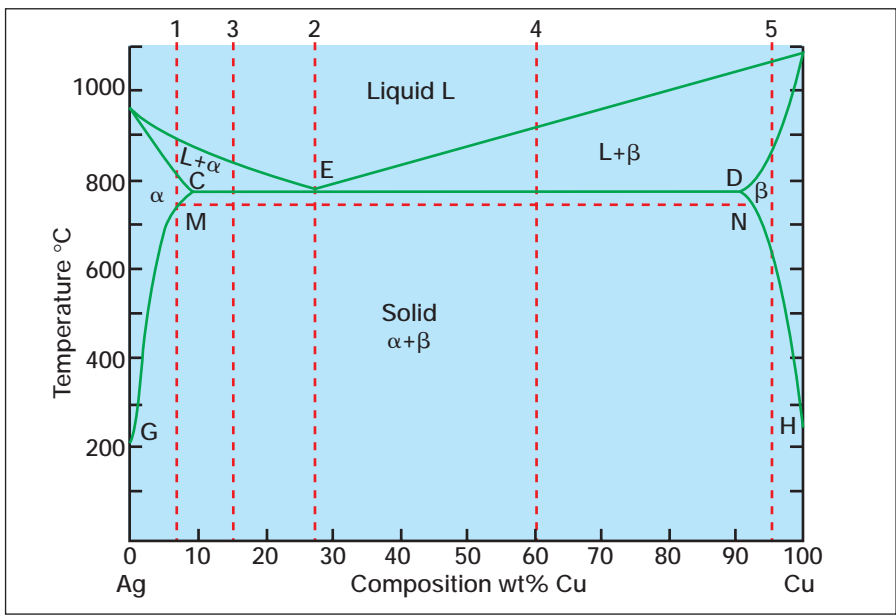


Figure 11 - Solidification of alloys in the silver-copper system under equilibrium conditions

different slope are affected by the quantity of liquid or solid transforming. If this is small, the arrest will be small also. Fortunately, other more sophisticated techniques are available to assist in defining transformation temperatures and phase boundaries. These include differential thermal analysis (DTA), X-ray diffraction (XRD) analysis and metallographic examination. However, the principles of construction remain the same.

Interpretation of alloy solidification

Let us now examine the equilibrium cooling from the melt to form a single-phase solid solution. A hypothetical binary system between Metal A and Metal B is used to clarify the explanation. The phase diagram, which is of the same form as the Au-Ag system but with a wider solidification range, is shown in Figure 10. Consider an alloy of composition, say, 40% A and 60% B.

Let us now consider the equilibrium solidification of alloys in the silver-copper (Ag-Cu) system, Figure 11. Alloy 1 is the well-known sterling silver composition of 92.5 wt.% Ag - 7.5 wt.% Cu. It starts to solidify at about 900°C and the first solid to form is the α -solid solution of composition 97% Ag - 3% Cu. Solidification is complete when the vertical composition line crosses the solidus at ~800°C, i.e. the solidification range is about 100°C. The solid has reached 92.5% Ag - 7.5% Cu by diffusion and is single-phase α -solid solution. The temperature continues to fall to 750°C where the α -phase can no longer tolerate so many copper atoms in the crystal lattice. It can be seen that the vertical composition line is crossing the boundary indicating the limit of solid solubility at M. It enters the two-phase field ' $\alpha + \beta$ ' and this means that crystals of the β -phase are forming within the α -phase. The composition of the β -phase is found by taking the tie line across the two-phase field to the other phase boundary at N where the composition is about 5% Ag - 95% Cu. As the temperature continues to fall, some more β -phase is formed and the compositions of the α - and β -phases change along the lines MG and NH, respectively.

Alloy 2 is the eutectic alloy. Solidification starts and is completed

at the eutectic temperature of 779°C. The solid being formed is a mixture of the crystals of α and β . Their compositions are given by the tie line CED and are 91.2% Ag - 8.8% Cu and 8% Ag - 92% Cu, respectively. Again, as the temperature falls, the compositions of the two phases will change along the lines CMG and DNH respectively.

Alloy 3 has the composition 85% Ag - 15% Cu. Solidification starts at ~850°C with α -phase of composition 96% Ag being formed. Just above 779°C, the structure is liquid of composition 71.9% Ag - 28.1% Cu and solid α of 91.2% Ag - 8.8% Cu although the overall composition remains at 85% Ag - 15% Cu. When crystals of pure metals or solid solutions grow from their nuclei, they usually do so by a dendritic growth mechanism (2). Dendrites have a characteristic branch-like structure. Therefore, there are dendrites of α surrounded by the liquid phase. At 779°C, the remaining liquid now undergoes the eutectic reaction and the α dendrites become surrounded by an intimate mixture of α and β crystals. The first solid phase to form is often referred to as the **primary phase** and so, in this case, the microstructure consists of primary dendrites of α surrounded by the eutectic mixture of $\alpha + \beta$.

Alloy 4 at 40% Ag - 60% Cu solidifies in a manner similar to that of Alloy 3 except that the structure will consist of primary dendrites of the β -phase surrounded by the same eutectic mixture of $\alpha + \beta$. Alloy 5 at 5% Ag - 95% Cu will form a single-phase β solid solution on reaching the solidus at ~960°C. On further cooling to ~750°C, crystals of the α -phase will precipitate out in the matrix of the β -phase.

The Lever Rule

The relative amounts of each phase in a two-phase field can be estimated using the **Lever Rule**. Consider the binary diagram in Figure 12. It is a eutectic system with an ' $\alpha + \beta$ ' two phase field. The Alloy X solidifies to the primary α -solid solution in a eutectic mixture of $\alpha + \beta$. Suppose we want to know the compositions and the relative proportions of the two phases at temperature T_1 shown by the tie line PQR. The compositions

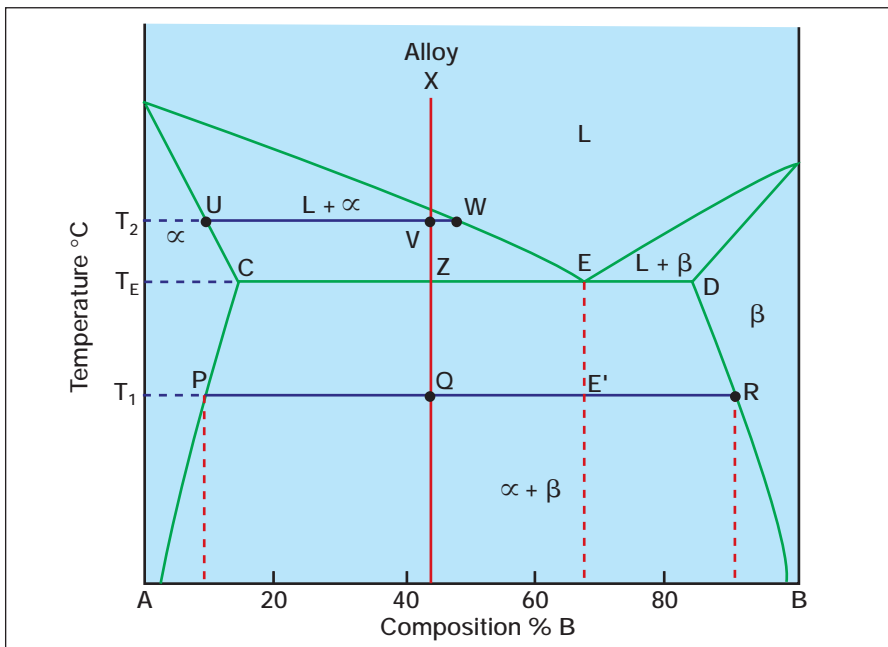


Figure 12 - The Lever Rule for estimating the amounts of each phase

are given at each end of the tie line by dropping down to the composition axis from P and R. The Lever Rule states that the proportion of α to β is given by

$$\frac{\alpha}{\beta} = \frac{QR}{PQ}$$

where PQ and QR are the relative lengths along the tie line.

An alloy composition has been selected that contains more of Metal A than Metal B. Intuitively, one should expect that this alloy contains more of the α -phase than the β . The Lever Rule demonstrates that this is true since QR is the greater length. The Lever Rule is easily proved (2) although we shall not include the proof here.

The diagram may be used for other examples of the Rule. For instance, at temperature T_2 ,

$$\frac{\text{Amount of liquid L}}{\text{Amount of solid } \alpha} = \frac{UV}{VW}$$

Just above the eutectic temperature T_E ,

$$\frac{\text{Amount of liquid L}}{\text{Amount of solid } \alpha} = \frac{CZ}{ZE}$$

but note that the liquid has now reached the eutectic composition given by the composition axis. We know that solidification of this liquid produces a eutectic mixture of α and β and the Rule tells us that their relative proportions in the mixture are given by

$$\frac{\alpha}{\beta} = \frac{ED}{CE}$$

At temperature T_1 , we have said that $\alpha/\beta = QR/PQ$, but the α -phase consists of both primary and eutectic α . Therefore, we can also say that

$$\frac{\text{Amount of primary } \alpha}{\text{Amount of eutectic } \alpha + \beta} = \frac{QE'}{PQ'}$$

Hume-Rothery Rules

The question may be asked, "Why do some alloy systems display a complete series of solid solutions whereas others show limited solid solubility?" Similarly, "Why do some systems have intermediate phases based around certain composition

ranges?" An eminent metallurgist, Professor W. Hume-Rothery, and his co-workers formulated the Hume-Rothery Rules, which answer such questions. Two of these rules are easy to understand. First, it should be obvious that, in order to form a complete series of solid solutions, the metals must have the same crystal lattice structure. Two face-centred cubic metals may form a complete series of solid solutions, although not necessarily so, but it would be impossible for this to occur if one metal has a face centred cubic structure and the other is either body centred cubic or hexagonal close packed. A fuller explanation of crystal lattice structure may be found in Reference 3. Secondly, there is an atomic size factor. If the diameters of the solvent and solute atoms differ by more than 14%, the solid solubility will be limited because the strain in the lattice in trying to incorporate solute atoms of a greatly different size becomes excessive.

There are two other important factors, namely, 'the electrochemical factor' and 'the relative valency factor' which also will affect the limit of solid solubility and the likelihood of intermediate phase formation (4) but further discussion is outside the scope of this paper.

Other features of binary phase diagrams

a) Miscibility Gap

The gold-nickel (Au-Ni) alloy system is an example of a system that displays a miscibility gap in the solid

state, Figure 13. There is a complete series of solid solutions at elevated temperatures below the solidus. However, as the temperature falls, the single-phase α -solid solution begins to separate into two solid solutions, one of which is gold-rich and the other nickel-rich. By convention, these are referred to as α_1 and α_2 although care has to be taken when reading diagrams from different publications as to which is which. The two phases become more Au-rich and Ni-rich as the temperature continues to fall. The appearance of the Au-rich phase explains why nickel-white golds have a yellowish tinge, particularly if they have been slowly cooled, and why they are often rhodium-plated to improve whiteness.

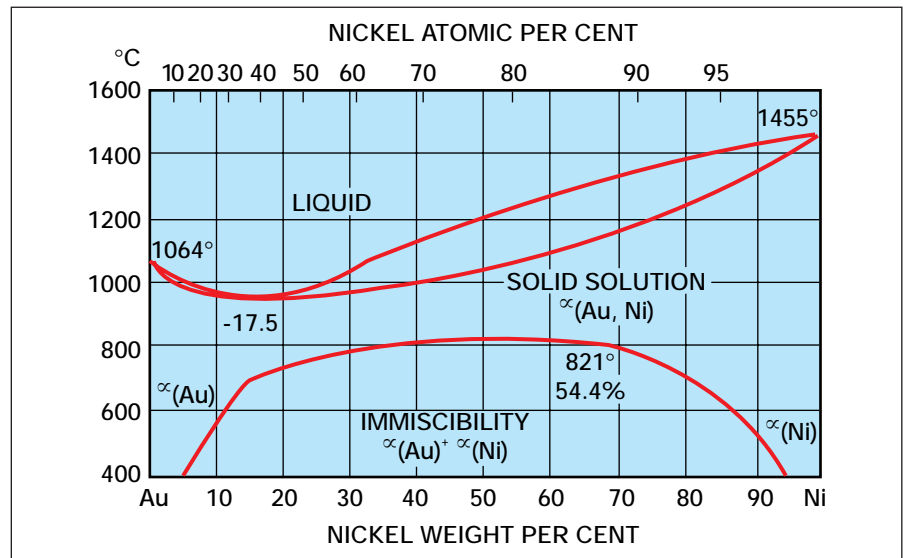


Figure 13 - Gold-nickel binary phase diagram

b) Peritectic reactions

A brief mention should be made of alloy systems that show a **peritectic reaction**, Figure 14. Consider the solidification of five alloys in the system Metal A-Metal B. Alloys 1 and 2 solidify to produce single-phase solid solutions α and β , respectively, as described earlier. Alloy 3 starts to solidify at S and crosses into the two-phase field, L + α . At point P, the compositions of the liquid and α phases are given by dropping to the composition axis from Q and R, respectively. The relative amount of L to α is PR:QP. All of the liquid reacts with all of the β -phase to produce a single-phase β solid solution. This is the peritectic reaction. However, almost immediately, the β -phase undergoes further transformation as α -phase begins to precipitate out in the β matrix to yield a two phase alloy.

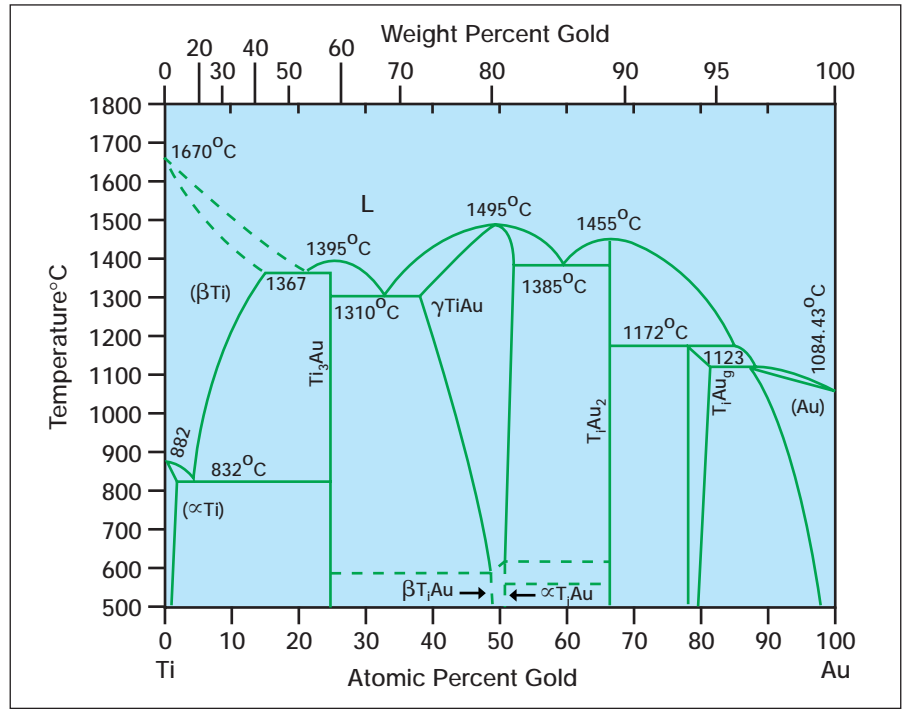


Figure 15 - Gold-titanium phase diagram

Alloy 4 produces primary α and at the peritectic temperature, all of the liquid reacts with some of the α to give a structure consisting of the excess primary α plus β from the reaction. Alloy 5 represents a case where some of the liquid reacts at the peritectic temperature with all of the primary α to give β -phase plus the

excess liquid, which will subsequently transform to β on further cooling.

c) Combinations

Many phase diagrams consist of combinations of the features described so far and may look very complicated at first sight. They are dealt with best by splitting them into their component sections so that each feature is considered in turn. Let us look at the gold-titanium (Au-Ti) binary system as an example, Figure 15. This happens to be plotted in terms of at.% composition (bottom axis). The shape of the diagram would be slightly different if it was plotted in wt.% but it would contain the same phases and phase fields and the interpretation would be the same.

There are partial solid solutions based on the parent metals. This diagram uses α to denote the Ti-rich solution because it has been drawn with Ti on the left and the Greek letters move from left to right. [Remember that some published Au-Ti diagrams may be drawn the other way round and the Au-rich solid solution may be referred to as the α -phase]. Titanium exists in two crystalline forms: It has a hexagonal closed packed lattice up to 882°C,

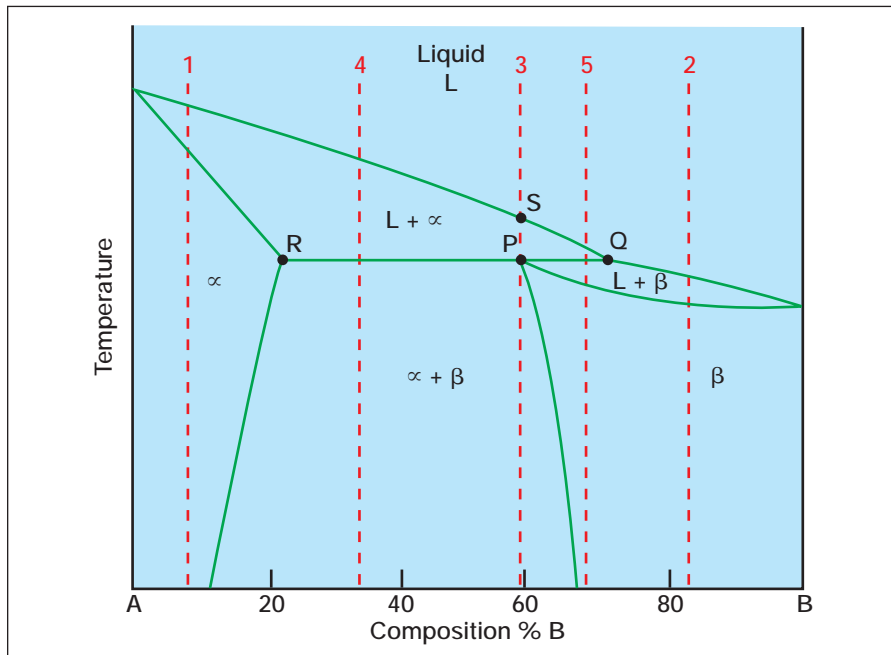


Figure 14 - Phase diagram showing a peritectic reaction (schematic)

which gives the α -solid solution with gold, and a body-centred cubic lattice from 885°C to the melting point of 1660°C, which accounts for the β -solid solution. This behaviour of changing crystal lattice structure is known as **allotropy**. You will note that the β structure can 'dissolve' much more gold and has a higher limit of solid solubility. Incidentally, the diagram tells us that at ~5 at.% Au and 840°C, there is a reaction which looks like a eutectic reaction except no liquid is involved. This is known as a **eutectoid** reaction and crossing the eutectoid temperature tie line from the single-phase field into the two-phase field gives the reaction $\beta \rightarrow \alpha + \text{Ti}_3\text{Au}$.

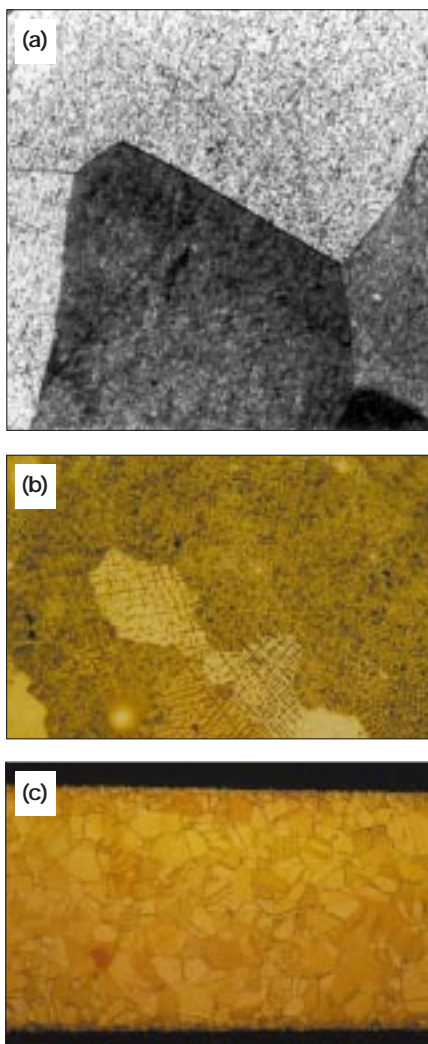


Figure 16 -
 (a) Microstructure of pure gold in the as cast condition x100 magnification
 (b) Microstructure of as cast 21 carat yellow gold - 4.5% silver-8.0% copper alloy x100
 (c) Microstructure of 21 carat yellow gold in wrought and annealed condition x100

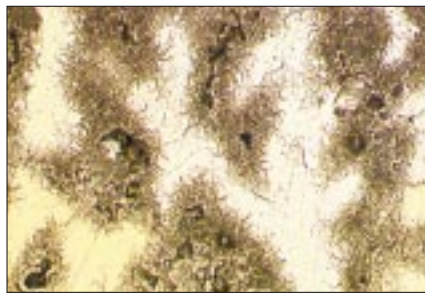


Figure 17 - Precipitation of β phase from the α phase

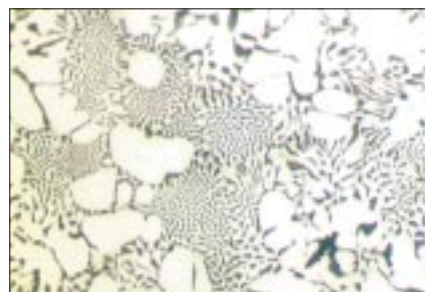


Figure 18 - Microstructure of eutectic

There are four intermediate phases based on intermetallic compounds, namely, Ti_3Au at 25 at.% Au (3:1 atomic ratio), TiAu around 50 at.% Au (1:1), TiAu_2 at 66.7 at.% Au (1:2) and TiAu_4 around 80 at.% Au (1:4). Ti_3Au and TiAu_2 exist as single phases only at fixed compositions - known as their **stoichiometric compositions**. The other two are single-phases existing over ranges of composition although these are small at low temperatures. There is a eutectic reaction in the section $\text{Ti-Ti}_3\text{Au}$; a second eutectic in the section $\text{Ti}_3\text{Au-TiAu}$ and a third eutectic in the section TiAu-TiAu_2 . Finally, there are two peritectic reactions in the section $\text{TiAu}_2\text{-Au}$. The first of these is $\text{L} + \text{TiAu}_2 \rightarrow \text{TiAu}_4$ and the second is $\text{L} + \text{TiAu}_4 \rightarrow$ the gold-rich solid solution. Each of the four sections can be treated in its own right as a binary diagram

Microstructure and metallographic examination

Mention has been made of the fact that metallographic examination can assist the construction and interpretation of phase diagrams. Metallurgists know what types of microstructure to expect in single and two-phase alloys. For example, a polycrystalline single-phase microstructure is obtained when a pure metal solidifies as is shown in

Figure 16a for pure gold. It is polycrystalline because each crystal has grown from a nucleus and many nuclei form at the start of solidification. The only difference is that although the crystal lattice is the same for each crystal, the orientation of lattice planes and directions vary from crystal to crystal and, therefore, boundaries are formed between them. Metallurgists tend to use the terms 'grain' and 'grain boundary' instead of crystal and crystal boundary and this must not be confused with 'grain' when it denotes the granular form of metals used to weigh out proportions for alloying. The grain size (crystal size) is affected by the number of nuclei and this in turn is influenced by initial temperature of the melt, i.e. superheat, the rate of cooling, and the presence, or otherwise, of any impurities.

Single-phase solid solutions will have a similar polycrystalline microstructure provided they have been cooled sufficiently slowly during and after solidification to approximate to equilibrium conditions (see next section). Figure 16b shows the structure of a cast 21 ct gold alloy (etching has revealed the dendritic structure within the grains due to coring). This paper is not directly concerned with working and annealing. However, it is worth pointing out that microstructures of wrought and annealed single-phase metals and alloys are the same in principle but are recognisable in comparison with the cast structures. This is because the grain size tends to be smaller, the grain boundaries are straighter and the grains may contain parallel-sided bands known as annealing twins, Figure 16c.

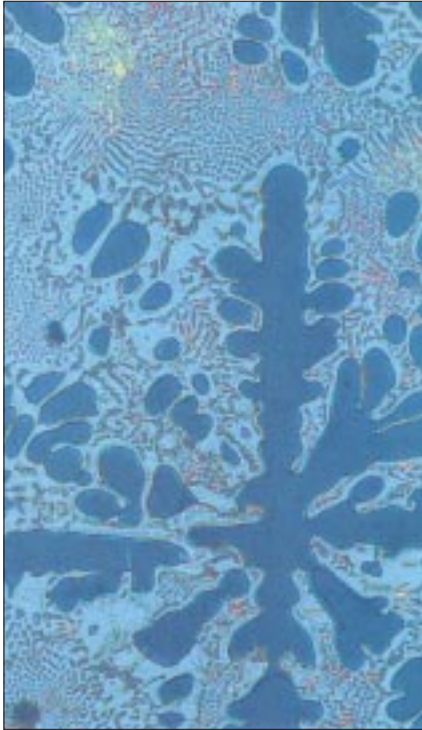


Figure 19 - Microstructure of silver-copper alloy showing primary β plus eutectic $\alpha + \beta$

The sizes and distribution of individual phases in multi-phase structures depends on the sequence of transformations during solidification and cooling. For example, if the alloy solidifies to a single-phase α -solid solution and then enters a two-phase field by the precipitation of a second phase β , the initial structure is that as described in the paragraph above. The precipitating β -phase will then appear in the grain boundaries and within the grains, usually on certain preferred crystal planes, in the α -phase, Figure 17. Binary eutectic alloys produce an intimate mixture of two-phases with small crystal sizes although the exact form of the microstructure depends on the position of the eutectic composition and whether one phase predominates. Figure 18 shows the silver-copper eutectic (28.1 wt.% Cu).

Single-phase metals and alloys usually solidify by the dendritic growth mechanism. This is not evident in the final microstructure because the spaces between the growing dendrite arms are eventually filled as the remaining liquid solidifies. Alloys which have solidified to produce a primary solid solution surrounded by, say a eutectic mixture, show a dendritic structure because the liquid trapped between the arms transforms to the

eutectic rather than the same primary phase, Figure 19. The grain size and pattern is often revealed by the different orientations of the primary dendrites.

Non-equilibrium cooling

Phase diagrams are very useful in giving a guidance to the microstructural condition of alloys at various temperatures and compositions but it must be remembered that it is assumed that equilibrium conditions exist. In practice, cooling rates during solidification or after heat treatment at elevated temperatures may be such that equilibrium conditions are not attained. This can lead to the presence of non-equilibrium phases in the microstructure. One example is 'coring', which is the variation in composition within a single-phase. It occurs when there is insufficient time for diffusion to even out the composition between the first and last single-phase solid to form during solidification. The sequence of steps leading to coring is described using Figure 20.

Consider an alloy of composition X. Solidification starts at point M, temperature T_1 , and the first solid α -phase nuclei have a composition given at point N. At temperature T_2 , instead of the composition of the solid being uniform at point O, as it

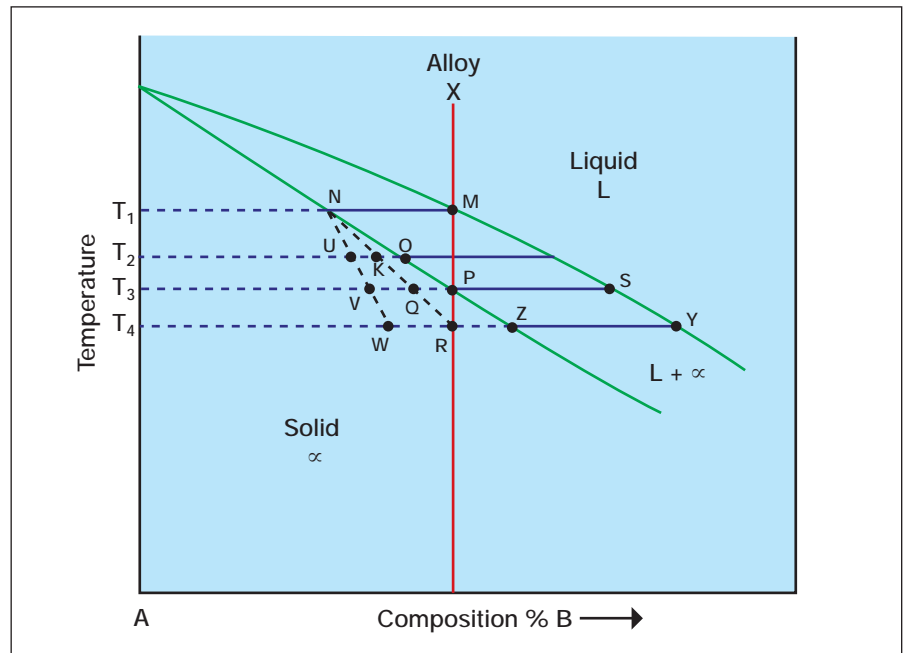


Figure 20 - Non-equilibrium cooling, leading to coring in solid solutions (schematic)

would be under equilibrium, the composition of the first solid to form has only changed slightly by diffusion to that at U. The new solid α forming on the nuclei has a composition indicated by O. The average solid composition is between O and U at K. Similarly, at temperature T_3 , where solidification is normally complete under equilibrium conditions, the original solid at the centre of the growing dendrites has only changed to V. The solid being formed on the outside of the dendrites has composition given by P and the average solid composition is at Q. It follows that the average solid composition is richer in Metal A than the overall composition. To counterbalance, there must still be some liquid present with a composition richer in Metal B, i.e. given by S. Solidification will not be complete until the average solid composition reaches the overall composition X at point R, temperature T_4 , which is lower than the equilibrium solidus temperature. The last drop of liquid to solidify has a composition given by Y and the last solid to form completing the polycrystalline structure has a composition given by Z.

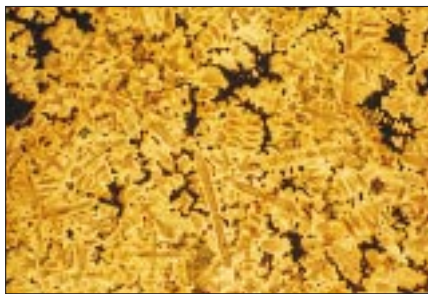


Figure 21- Coring in a cast 18 carat gold



Figure 22 - Cast sterling silver showing non-equilibrium microstructure of primary α surrounded by some eutectic $\alpha + \beta$

There is now a composition gradient ($W \rightarrow Z$) across the dendrite arms from the first solid α to form at the centres to the last at the edges. The dendritic growth mechanism may be obvious in the microstructure because the composition gradient may show up as colour variations across the dendrite arms, Figure 21. This is true particularly for gold- and copper-base alloys where alloying constituents affect the colour of the parent metals.

Other non-equilibrium structures may be found in systems with eutectic and peritectic reactions. A very good example is sterling silver at 92.5% Ag and 7.5% Cu. The equilibrium phase diagram, Figure 8, indicates that it should solidify to single-phase α solid solution before subsequently precipitating out the β -phase. In practice, because often there is still some non-equilibrium liquid phase present when casting, this will undergo the eutectic reaction when the eutectic temperature of 779°C is reached. The non-equilibrium microstructure will consist of primary α surrounded by a small amount of eutectic $\alpha + \beta$ Figure 22.

Coring and other non-equilibrium structures may be removed by long-term heating at elevated temperatures just below the solidus. This promotes diffusion and the homogenisation of compositions.

Non-equilibrium structures are obtained also when alloys are **quenched** from temperatures and compositions within a single-phase solid solution field. The term '**quenching**' implies that the cooling rate is sufficiently fast to prevent the normal equilibrium phase changes from occurring so that a **supersaturated solid solution** is retained at lower temperatures. This will be discussed more fully in a later section under heat treatment. However, this has an important consequence for carat gold alloys below 21ct containing copper. They should always be quenched from the single-phase α field to prevent ordering and other precipitation processes if further working is envisaged since maximum softness and ductility is only achieved in the supersaturated condition.

The next part of this paper will

describe ternary phase diagrams and, in particular, the gold-silver-copper system which is the basis for the coloured carat golds. The use of phase diagrams in predicting structural and property changes and alloy design for jewellery manufacture will be discussed with appropriate examples.

References (Part One)

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Editor's note: Many binary phase diagrams of gold alloys are available in the book, "Phase Diagrams of Binary Gold Alloys", Ed. H. Okamoto and T.B. Massalski, publ. in 1987 by ASM International, Metals Park, Ohio 44073, USA. ISBN no. 0-87170-249-5.

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