BASIC METALLURGY OF THE PRECIOUS METALS: PART 1 - EFFECT OF ALLOYING ON PROPERTIES

Dr. Christopher W. Corti

The aim of this series of ‘Basic Metallurgy’ presentations is to help jewelers better understand the science and technology that underpins the manufacture of jewelry in their industry, be it by traditional handcraft techniques or by mass manufacture on machines. This is important if they are to produce good product efficiently and avoid defects and other problems that impact quality, time taken and especially costs. In Part I, we look at how alloying affects the properties of the jewelry precious metals and the influence of working and annealing on these properties.

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INTRODUCTION

Since the early days of the Santa Fe Symposium®, there have been presentations on the basic metallurgy of the precious metals. One of the most notable speakers has been Mark Grimwade. Indeed, he first went to print on the subject back in 1979 with his series of articles in the old Aurum magazine, many of which were reprinted in early issues of Gold Technology. He has since published the 2nd edition of his book1, 'Introduction to Precious Metals' in 2009. These publications stand as testimony to Mark's extraordinary ability to explain in simple terms the basics of metallurgy for the non-metallurgist and how it can be used for practical benefit by practicing jewelers, goldsmiths and silversmiths and the like.

The need for such knowledge has been demonstrated to me many times during seminars on jewelry technology around the world. In this presentation, the first in a series of 4 or 5 parts, I try to provide a basic understanding of the precious metals and their metallurgy to serve as a basis for those practicing the art and technology of jewelry manufacture. In doing so, I acknowledge the contribution of Mark, whose approach to the topic has influenced and molded my own.

WHAT USE IS KNOWLEDGE OF BASIC METALLURGY?

Whatever craft or profession one pursues - be it art or science and technology or engineering - one needs to understand the nature of the materials used and the characteristics of the tools used to fashion them into objects of art or function that are 'fit for purpose' and aesthetically pleasing. Jewelry-making is no exception. It embraces both art and technology. The aim of this Basic Metallurgy series, therefore, is to give an appreciation of the basic metallurgy of the precious metals used in jewelry:

- To assist jewelers in developing an appreciation of the physical, chemical and metallurgical nature of the metals and alloys with which they work.
- To understand how alloying affects the properties of the precious metals – color, strength, malleability, melting range, etc. – as well as emphasizing why they occur in terms of changes in the microstructure and its influence on properties.
- To understand what happens when a metal or alloy is worked and deformed and why annealing is necessary to prevent overworking and to restore ductility, again in terms of the microstructural changes that occur.
- To assist in recognizing the causes of defects and failures that can occur when metals are cast or worked and how they can be prevented or remedied.

In this first presentation, I will focus on the effect of alloying on properties of all the four major precious metals used in jewelry – gold, silver, platinum and palladium. Because of the breadth of its alloys and its unique color characteristics, I will focus particularly on gold to illustrate the basic metallurgy involved. However, it is applicable to all 4 metals and their alloys. However, I first need to explain some basics about the nature of metals and alloys.

THE NATURE OF METALS

The properties of metals and alloys are dependent on their chemical composition, their microstructure and processing history. They are all interrelated. Whilst used primarily for decoration, jewelry alloys are engineering materials and follow the same ‘rules’ of science as aerospace and construction materials! To make good jewelry, a jeweler should understand the materials he/she uses. In this series of presentation, we look at the properties of the precious metals and how they are influenced by alloy composition and microstructure. What happens when we deform – or work - them and when we anneal worked material? How can we get the best properties from them, suited to the processes we use or to optimize the finished article to the environment in which it will be used?

The Chemical Elements

All jewelers should understand the basic nature of the jewelry alloys they use. The pure metals are part of the collection of chemical elements found in nature. The first basic fact that one should appreciate is that the smallest particle of a chemical element is called an atom and that this is composed of a nucleus of protons and neutrons surrounded by a cloud of electrons that orbit around the nucleus. The atoms of each chemical element are identical but different from other chemical elements in size and weight ('mass'), because they have differing numbers of protons, neutrons and electrons. The chemical elements can be arranged in order of size and characteristics into what is known as the Periodic Table. In each vertical column of the Table, the elements share similar characteristics. Thus, in Group 8, nickel, palladium and platinum share similar characteristics as do copper, silver and gold in the adjacent Group 1B column. Some chemical elements are classed as metals and others are classed as non-metals.

The second point to appreciate is that (nearly) all metals and alloys are crystalline in the solid state, just like gemstones and minerals. The atoms are packed in a regular array in what we call a crystal lattice. Imagine a cardboard box packed carefully with tennis balls in an ordered array. We can pack them in various ways, each ball touching some neighbors. Some ways of packing are more space-efficient than others, i.e. packed closer together.

Packing of atoms: The way that the atoms pack together is important as it influences their properties, e.g. how easily they deform during working and how ductile they are. Most metals and alloys pack their atoms in one of three basic configurations, Figure 1:

- Face-centered cubic (FCC)
- Body-centered cubic (BCC)
- Close-packed hexagonal (CPH)

There are other configurations, but these are the most common. Interestingly, all our four precious metals – gold, silver, platinum and palladium – are face-centered cubic (FCC). This structure is the most easily deformed and the most ductile. At the other extreme, metals like zinc, magnesium and ruthenium are close packed hexagonal (CPH) and have limited deformability and ductility. Others, such as iron, chromium, molybdenum and ferritic steels are body-centered cubic (BCC) in structure, but this may depend on the temperature. Iron and many steels are BCC at low temperature ('ferritic') but transform to FCC ('austenitic') at higher temperatures and even revert to BCC just before they melt. Other metals, such as tin and titanium, also change structure with temperature, titanium changing from CPH to BCC at about 885°C (1625°F).

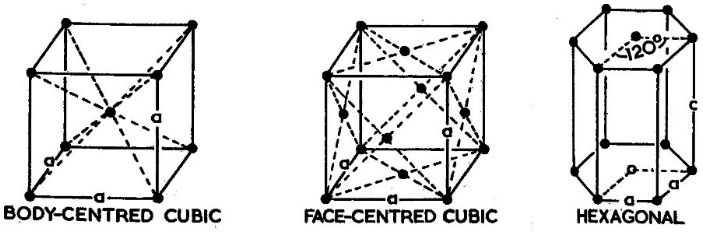
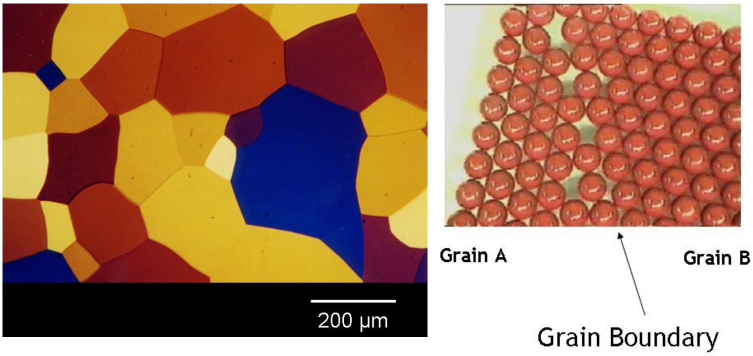


Figure 1: Typical crystal structures of metals (left to right): body-centered cubic, face-centered cubic and close-packed hexagonal

In practice, real metals and alloys are made up of lots of small crystals – or grains as the metallurgist calls them. They are polycrystalline, with each crystal (or grain) facing (oriented) in different directions, Figure 2a. Because of this, the atoms do not neatly fit the crystal lattice across the boundary between them, Figure 2b. Such boundary regions are known as crystal or grain boundaries and these can be lines of weakness and preferred sites for deleterious impurities, causing embrittlement and thus a tendency to easily crack. As we shall see later, the crystal or grain size affects properties, and we try and control it in jewelry manufacture.



(a) (b)

Figure 2: Schematic: (a) A polycrystalline alloy (the color shades indicate the different orientations of the crystals) (b) The different orientation of adjacent crystals leads to a poor matching of atoms across the grain (crystal) boundary

What is a metal? The characteristics of pure metals (and alloys too) include the following:

- Good thermal and electrical conductivity
- High surface reflectivity (polish or lustre)
- Malleable (good ductility, capable of being heavily deformed)
- Heavy, i.e. high density
- Toughness
- Reasonable strength and hardness

These do not, however, define what metals are and are misleading to some extent. Some metals have low densities (e.g. magnesium, lithium, aluminum) and non-metals like carbon (graphite) have good thermal and electrical conductivity. Alternatively, we might define them as chemical elements that form the positive ions in chemical compounds, such as sodium (Na^+) in sodium chloride ($NaCl$), but even that is not without exceptions: gold and zinc, for example, form aurates and zincates respectively with some other metals under certain conditions. What really defines metals is the way their atoms bond together – by so-called 'metallic bonding'. Here the atoms are not so tightly held as in chemical bonding – 'ionic bonding' – or as in non-metals – 'co-valent bonding'. Metallic bonding enables electrons to flow easily, hence good electrical conductivity.

What is an alloy? When we talk of alloys, we mean a mixture of two or more pure metals. Brass is an alloy of copper and zinc, bronze an alloy of copper and tin, steel an alloy of iron and carbon (not strictly a metal) and other metals. An alloy may contain one or more phases in its microstructure. These may be differentiated by differences in chemical composition and/or crystal structure. Steel consists of iron (in various crystal forms) and second phases, usually carbides of iron and the alloying metals. Cast iron (gray), on the other hand, consists of iron and graphite.

Why Alloy? In general, the pure metals tend to be soft and not so strong, so alloying with other metals enables us to manipulate properties, typically to increase hardness and strength, but also other properties such as color, corrosion resistance, thermal expansion coefficient, temperature stability and magnetic properties to suit their application requirements.

Why are alloys stronger? Deforming Alloys: If we take a simple gold alloy as an example, we find that the alloying metal substitutes for some gold atoms in the gold crystal lattice (but it can get more complicated as we shall see later). We should recall that atoms of different metals have different atom sizes (diameters), so substituting atoms of silver (or other alloying metal) into the parent gold lattice causes a distortion of the crystal lattice, Figure 3. When we deform a metal, layers of atoms in each crystal slide over each other in a complex way to accommodate the overall shape change that we impose. We term this mechanism ‘slip’. How it does this, I will not discuss here, except to say it involves planar crystal defects called dislocations. It is rather complex, but one can appreciate that distorting the crystal lattice by alloying makes the crystal planes distorted and, hence, makes the slip mechanism more difficult, so requiring more force. Thus, the alloy is stronger, harder and more difficult to deform.

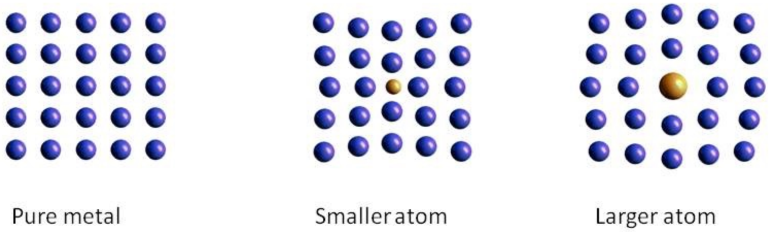


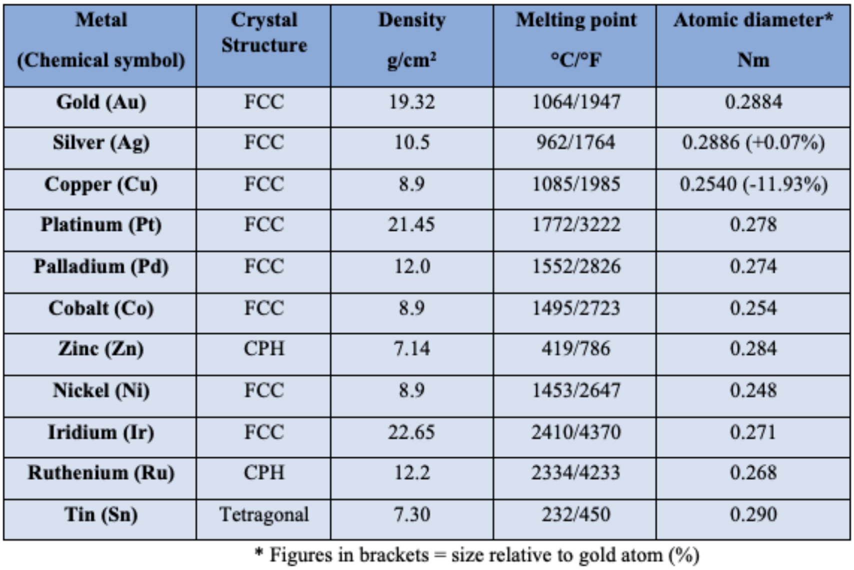
Figure 3: Distortion of the gold crystal lattice caused by substitution of atoms of an alloying metal due to its different atom size

If we have second phases present in the microstructure, these also hinder slip and give further strengthening, the amount depending on number and size of the second phase (finer equals stronger; we will discuss precipitation hardening later). As we deform a metal, the slip mechanisms cause the crystal to become less perfect with a growing accumulation of the defects known as dislocations. If we could restore the perfection of the crystals, we should restore ductility.

Table 1 lists some of the common metals used in precious jewelry alloys and some of their basic properties. Note, for example, that the copper atom is much smaller than the gold atom, whereas silver is slightly larger. As we shall see shortly, alloying gold with copper has a bigger effect on its strength and hardness than does silver, because it causes greater distortion of the gold crystal lattice and thus makes deformation more difficult.

Alloying can get more complex: often, we can only substitute a limited amount of alloying metals into the parent crystal lattice. At higher amounts, second phases of different chemical composition and/or crystal structure form to give two phase microstructures which generally lead to stronger, less ductile materials. How the second phases are distributed in the microstructure is also important. Working such alloys can also lead to a refinement of the microstructure in such alloys.

Table 1: Basic Properties of the Precious and Typical Alloying Metals



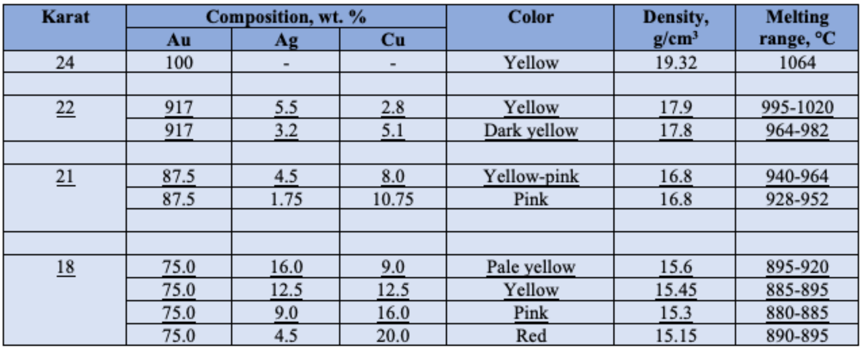
Metal (Chemical symbol)	Crystal Structure	Density g/cm^2	Melting point °C/°F	Atomic diameter* Nm
Gold (Au)	FCC	19.32	1064/1947	0.2884
Silver (Ag)	FCC	10.5	962/1764	0.2886 (+0.07%)
Copper (Cu)	FCC	8.9	1085/1985	0.2540 (-11.93%)
Platinum (Pt)	FCC	21.45	1772/3222	0.278
Palladium (Pd)	FCC	12.0	1552/2826	0.274
Cobalt (Co)	FCC	8.9	1495/2723	0.254
Zinc (Zn)	CPH	7.14	419/786	0.284
Nickel (Ni)	FCC	8.9	1453/2647	0.248
Iridium (Ir)	FCC	22.65	2410/4370	0.271
Ruthenium (Ru)	CPH	12.2	2334/4233	0.268
Tin (Sn)	Tetragonal	7.30	232/450	0.290

* Figures in brackets = size relative to gold atom (%)

DEFORMING METALS AND RESTORING DUCTILITY BY ANNEALING

I am not going to discuss this important process in this presentation but save it for Part II when we will examine the effect of casting, solidification and working on microstructure. However, I will just say that we can restore ductility of worked metals and alloys by heating them above a critical temperature for a given time. This process is called annealing and it involves changing the deformed crystals into undeformed new crystals by a mechanism called recrystallization. I will further note that how we cool the alloy after annealing – fast or slow - can also affect properties of the annealed material for some alloys. To understand why, we will need to explain about phase diagrams – the metallurgists ‘road maps’ of alloying behavior. But first, let’s look at some properties and how alloying affects them.

Table 2: Physical Properties of Typical Gold Alloys



Karat	Composition, wt. %			Color	Density, g/cm³	Melting range, °C
	Au	Ag	Cu			
24	100	-	-	Yellow	19.32	1064
22	917	5.5	2.8	Yellow	17.9	995-1020
	917	3.2	5.1	Dark yellow	17.8	964-982
21	87.5	4.5	8.0	Yellow-pink	16.8	940-964
	87.5	1.75	10.75	Pink	16.8	928-952
18	75.0	16.0	9.0	Pale yellow	15.6	895-920
	75.0	12.5	12.5	Yellow	15.45	885-895
	75.0	9.0	16.0	Pink	15.3	880-885
	75.0	4.5	20.0	Red	15.15	890-895

EFFECT OF ALLOYING ON PROPERTIES

Let's begin by looking at some typical properties of karat golds and see what we can learn. The colored karat golds are based on gold with additions of copper and silver, often with some other small additions such as zinc to control specific properties. (We will discuss white golds later.)

Physical properties: Table 2 shows some physical properties for gold –copper-silver alloys – the colored karat golds. We can see that density decreases as karatage decreases (not so surprising considering that gold has a much higher density than silver or copper), but at any particular karatage, the actual density depends on the relative amounts of the alloying metals, copper and silver (because they have different densities).

We also see that gold, a pure metal, melts or solidifies at a fixed temperature of 1064°C (1947°F). However, the alloys of gold melt over a temperature range. This temperature range also falls as karatage is lowered. All alloys, not only those of gold, melt or solidify over a temperature range, with a few special exceptions (such as eutectic compositions). The size of the melting range can influence the alloy structure on a micro-scale – the microstructure as we refer to it.

We also notice that color varies at each karatage level according to the relative amounts of silver and copper. In addition, we note that we can get a wider variation in color as karatage is lowered, as shown in Table 3 for a larger range of karatage. At 18K, as copper increases (i.e. silver decreases), we go from a green shade of yellow through pale yellow, yellow to pink (or rose) and red. At 9K and 10K, for example, the range increases further, with white appearing at high silver contents.

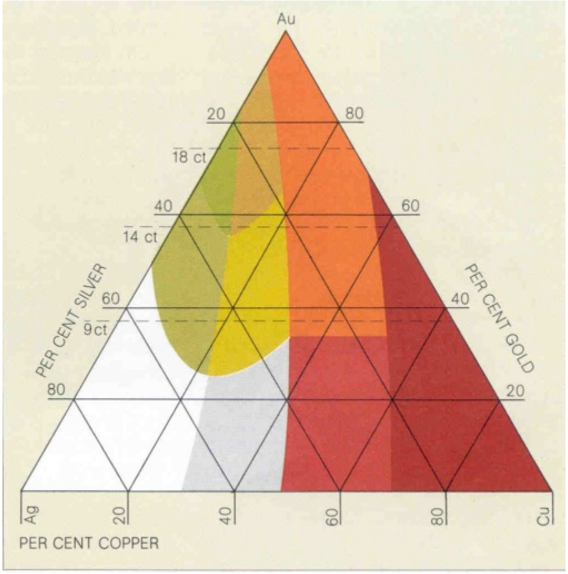
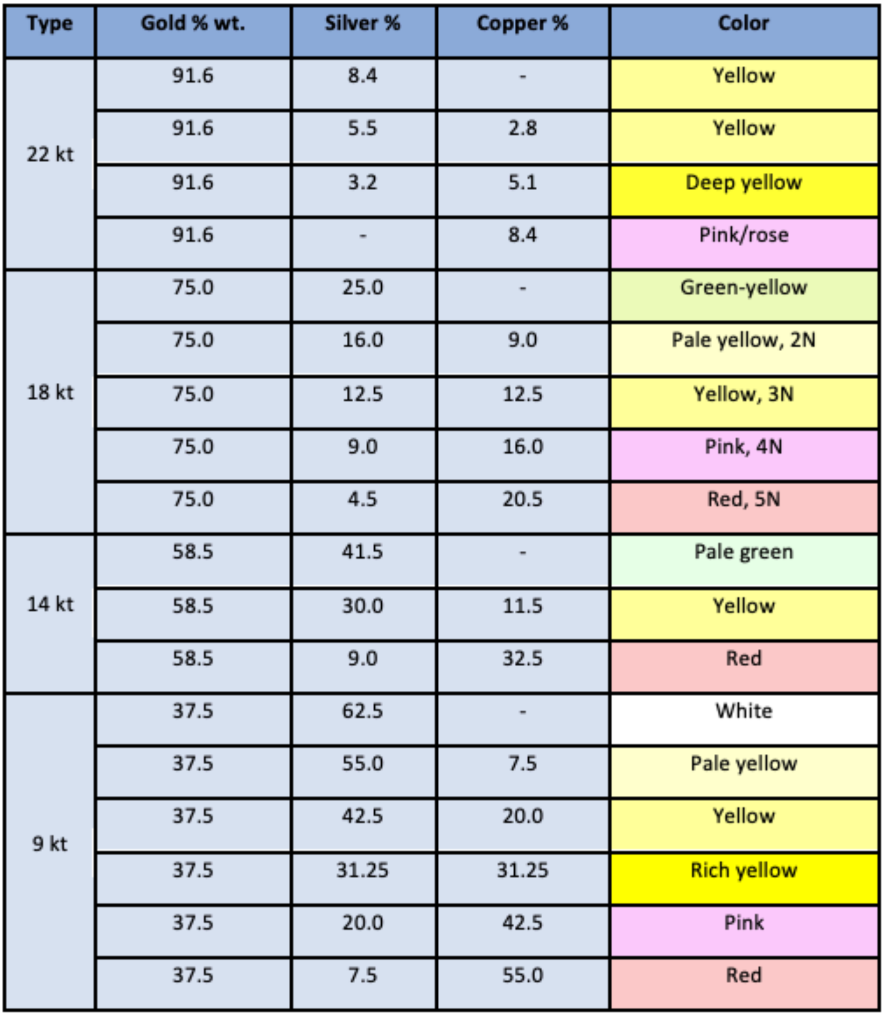


Figure 4: The gold-silver-copper "color triangle" showing the range of colors versus composition

We can illustrate the variation in color possible in gold-copper-silver alloys by the "color triangle", Figure 4. Here we show schematically all possible alloys and their color. Pure gold is at the top corner of the triangle, copper on the bottom right and silver on the bottom left. Horizontal lines illustrate the gold content for 18K, 14K and 9K on this triangle. At each karatage, all possible alloy compositions can be plotted. On the left side, we can see that if we come down to 9K, a gold-silver alloy is actually white. On the right side a 9K gold-copper alloy is very red, but we cannot get a good red at high carats, such as 22K. Alloys of gold containing both copper and silver lie between the two extremes on the appropriate lines at any karatage. The amount of each depends on the position on the line and is in proportion to the relative lengths of the lines either side of the point. The scope for changing color does increase with alloy content and this becomes even more apparent at the lowest karatages of 14K, 10K and 9K.

Table 3: Effect of Copper:Silver Ratio on Color of Karat Golds



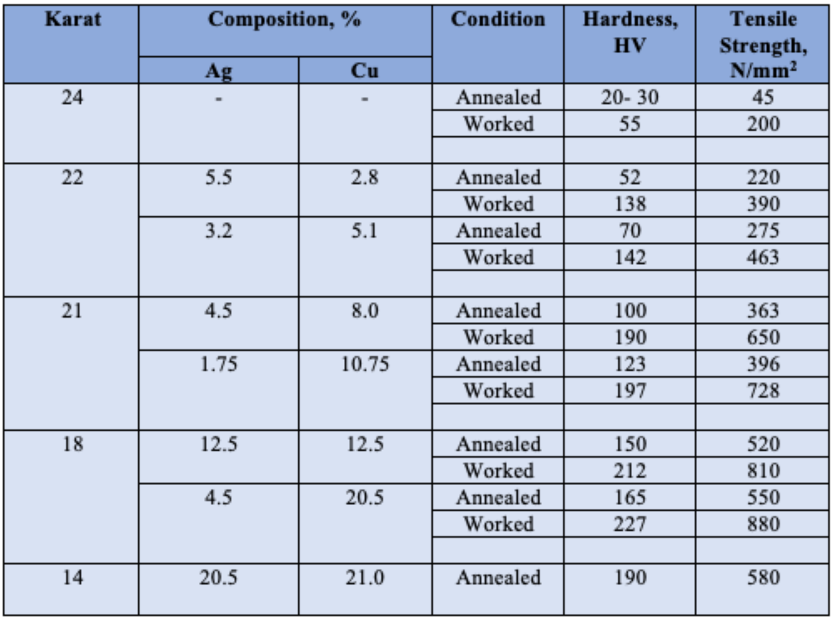
Type	Gold % wt.	Silver %	Copper %	Color
22 kt	91.6	8.4	-	Yellow
	91.6	5.5	2.8	Yellow
	91.6	3.2	5.1	Deep yellow
	91.6	-	8.4	Pink/rose
18 kt	75.0	25.0	-	Green-yellow
	75.0	16.0	9.0	Pale yellow, 2N
	75.0	12.5	12.5	Yellow, 3N
	75.0	9.0	16.0	Pink, 4N
	75.0	4.5	20.5	Red, 5N
14 kt	58.5	41.5	-	Pale green
	58.5	30.0	11.5	Yellow
	58.5	9.0	32.5	Red
9 kt	37.5	62.5	-	White
	37.5	55.0	7.5	Pale yellow
	37.5	42.5	20.0	Yellow
	37.5	31.25	31.25	Rich yellow
	37.5	20.0	42.5	Pink
	37.5	7.5	55.0	Red

Now let us turn to mechanical properties:

Mechanical properties: Table 4 shows the effect of alloying down to 14K on hardness and tensile strength. Figures are given for alloys in the soft, annealed condition and in the hard, worked (deformed) condition, in this case after 50% reduction in area. We can see that at each karatage level, working increases the hardness and strength; we shall come back to this shortly. We also notice that the hardness and strength of both annealed and worked alloys increases with increase in alloying content, i.e. as karatage is lowered. Finally, we can see that at any given karatage, copper is more effective than silver in strengthening gold. That is because there is a bigger difference in size between gold and copper atoms than between gold and silver atoms. Copper distorts the gold crystal lattice more, making it more difficult to deform the crystals or grains.

These aspects can be seen more clearly in Figure 5. We can see that gold-copper alloys are stronger than gold-silver alloys in both annealed and cold-worked conditions and that a gold-copper-silver alloy is stronger than gold-copper at lower karatages. Note that gold-copper alloys harden more than gold-silver alloys for the same amount of working.

Table 4: Mechanical Properties of Typical Gold Alloys



Karat	**Composition, %**		**Condition**	**Hardness, HV**	**Tensile Strength, N/mm²**
	Ag	**Cu**			
24	-	-	Annealed	20- 30	45
			Worked	55	200
22	5.5	2.8	Annealed	52	220
			Worked	138	390
	3.2	5.1	Annealed	70	275
			Worked	142	463
21	4.5	8.0	Annealed	100	363
			Worked	190	650
	1.75	10.75	Annealed	123	396
			Worked	197	728
18	12.5	12.5	Annealed	150	520
			Worked	212	810
	4.5	20.5	Annealed	165	550
			Worked	227	880
14	20.5	21.0	Annealed	190	580

As all goldsmiths know, as we work (deform) a material, it gets harder and stronger and more difficult to deform further, as we can see in this next schematic graph, Figure 6. How hard the alloy becomes on working depends on the alloy. Figure 6 illustrates one that hardens quickly (curve I) and another that hardens more slowly (curve II). We saw this difference in Figure 5 for gold-copper and gold-silver alloys.

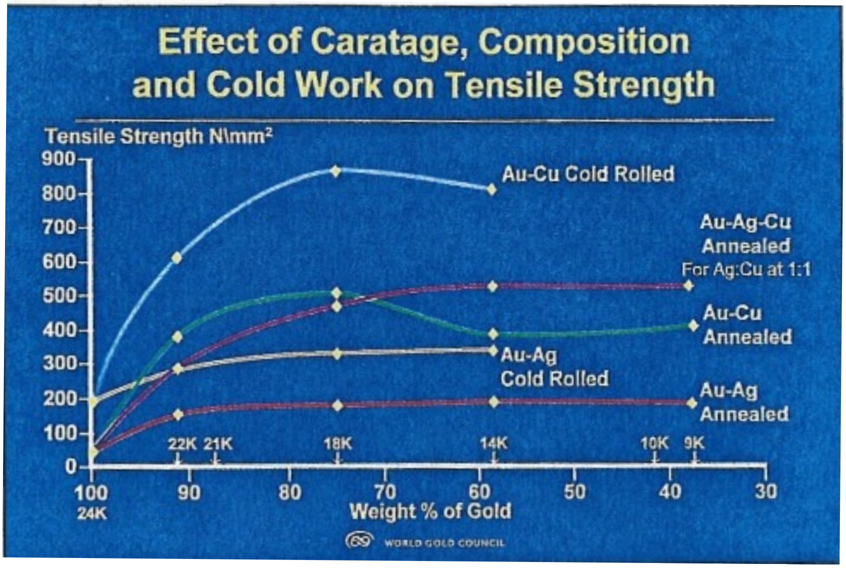


Figure 5: The hardness of gold-silver, gold-copper and gold-silver-copper alloys versus gold content

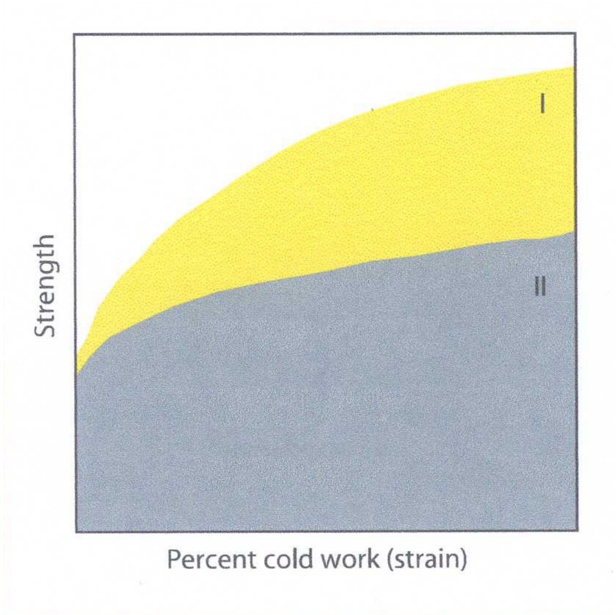


Figure 6: Schematic: Typical work hardening curves for alloys, showing difference in work hardening rates.
Curve I – hardens quickly, curve II hardens more slowly

PHASE DIAGRAMS AND ALLOY STRUCTURES: THEIR INFLUENCE ON MAKING JEWELRY

I have mentioned earlier about the metallurgist's 'Road Maps' – phase diagrams. These are simply diagrams of alloying behaviour, as a function of temperature and composition under equilibrium conditions (hence, their alternative name, 'equilibrium diagrams'). As some of you may know, additions of zinc can improve the workability of the low-medium karat golds and that we can age harden some alloys. These phenomena are explicable in terms of the phase diagrams, so let's take a brief look at what they are and how to understand them. They will seem very complicated to those of you not used to them, but I will try and navigate you through the important aspects. For those of you wanting a more detailed explanation, I recommend Mark Grimwade's articles in Gold Technology,[2] written with the layman in mind.

The simplest diagram to understand is the gold-silver diagram, Figure 7. In both liquid (molten) and solid states, gold and silver are mutually soluble at all concentrations. There are two lines on the diagram joining the melting points of gold and silver. The top one is called the liquidus, and above this all alloys are completely molten. The bottom line is called the Solidus and below this, all alloys are completely solid. Between these lines constitutes the melting range where liquid and solid co-exist.

If we take any alloy composition, say 50% silver, then on cooling the molten alloy, as it reaches the liquidus temperature, solidification commences and is completed as the solidus temperature is reached. Further cooling has no effect on structure. At all compositions, the microstructure is single phase solid solution. An additional point of interest: during solidification, the phase diagram can also tell us the composition of the metal solidifying. This varies as solidification progresses (temperature falls) and is the cause of microsegregation in cast metals.

The gold-copper diagram is a little more complicated, Figure 8. Note that both liquidus and solidus lines dip in the middle and actually touch at around 20 wt.% copper at a minimum temperature of 889°C/1632°F. The melting range is narrow over all compositions. In the solid state, above about 400°C/750°F, copper and gold are also mutually soluble at all compositions and so are single phase alloys. But below circa 400°C/750°F, we see some extra lines in two composition ranges. These indicate that the structure changes. There is a crystal structure change! Two ordered intermetallic phases are formed, AuCu and $AuCu_3$, and these new low temperature structures are stronger, harder and less ductile.

It is one of the reasons why we water quench 18K and lower karat golds that contain high copper contents after annealing – to prevent these less ductile phases forming.

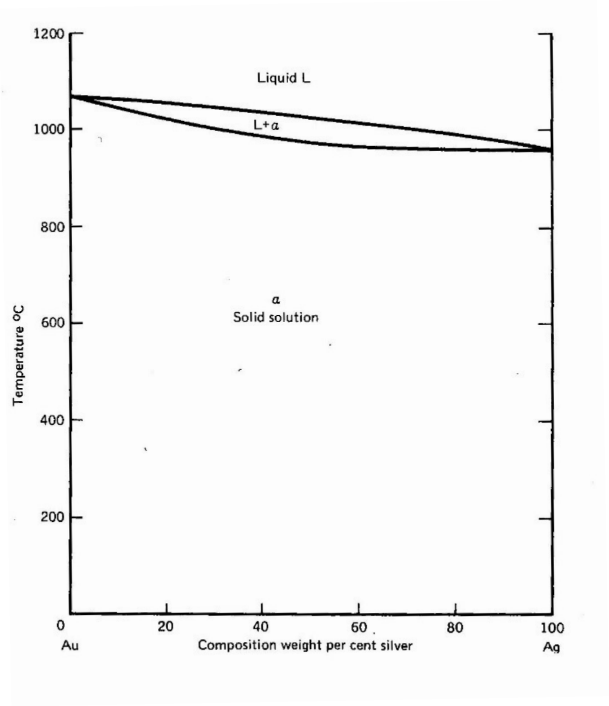


Figure 7: The gold-silver phase diagram

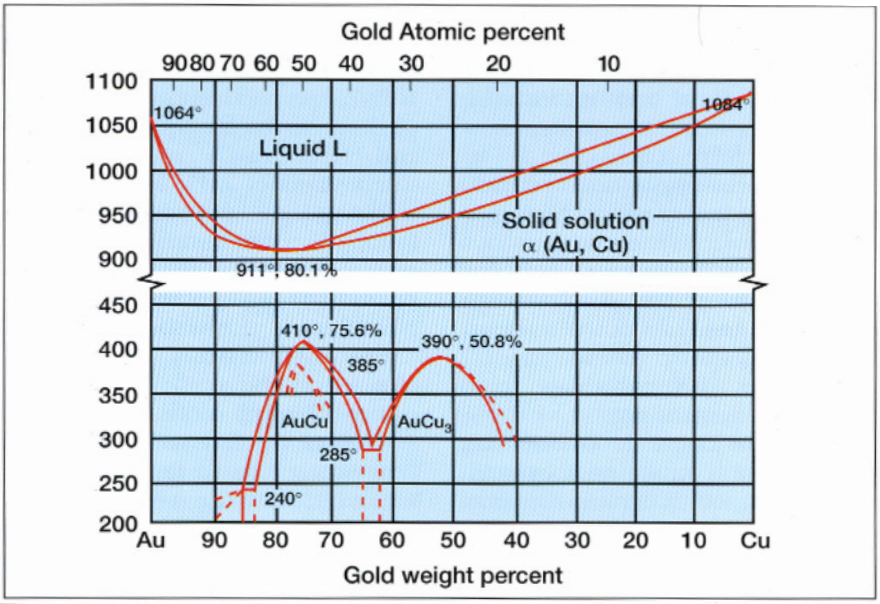


Figure 8: The gold-copper phase diagram

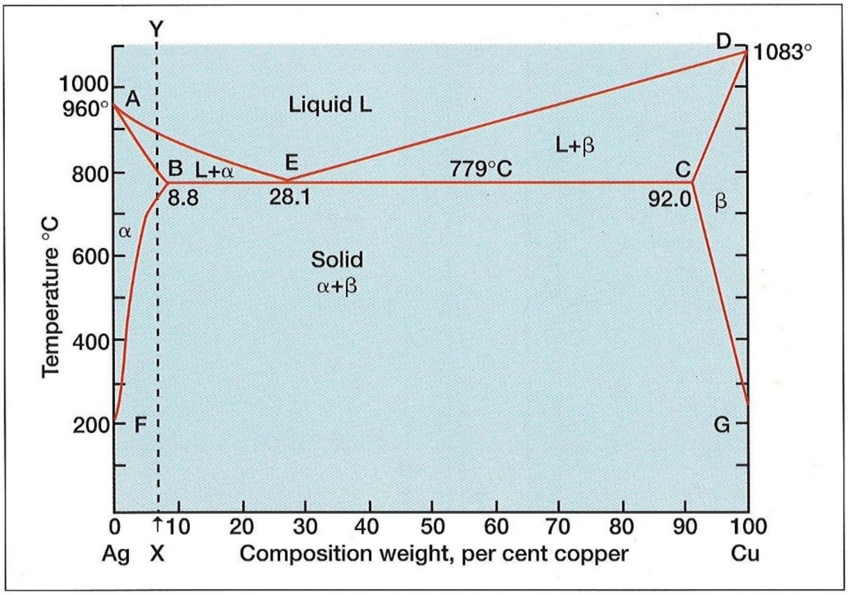


Figure 9: The copper-silver phase diagram

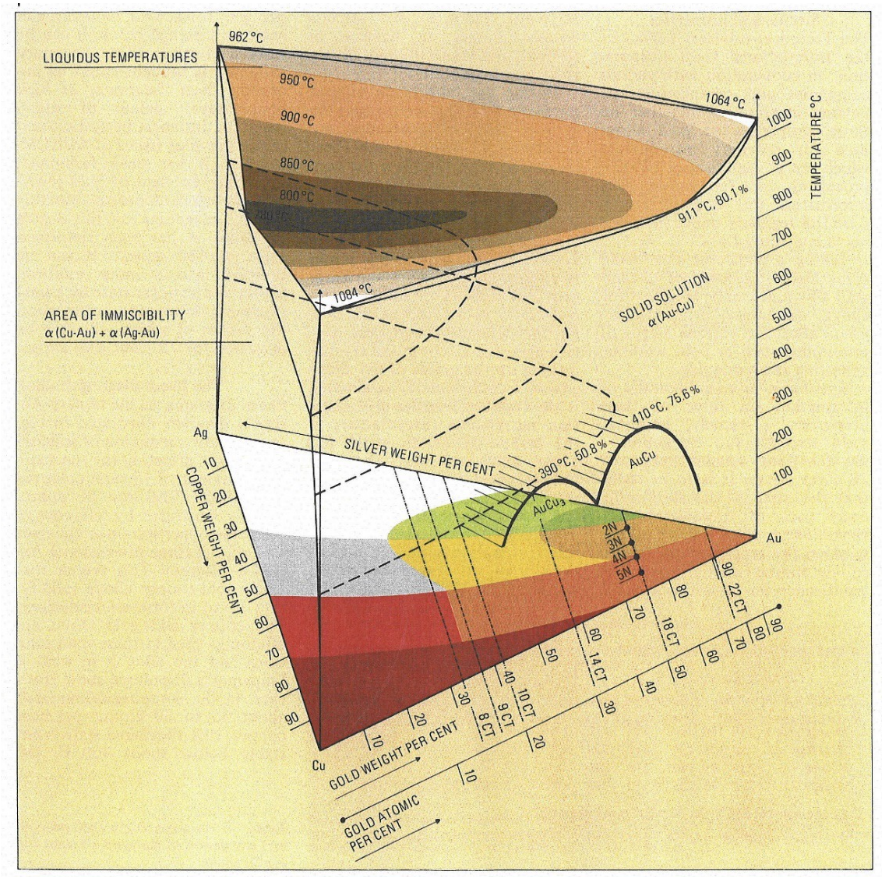


Figure 10: The gold-silver-copper ternary phase diagram

I am now going to show you the copper-silver diagram, Figure 9. You will see its relevance to karat golds shortly. The liquidus line is Line AED and the solidus line is ABECD. Here you can see that, in the solid state, copper and silver are mutually soluble in each other only to a limited extent. As a consequence, in the central region of composition, we end up with a two-phase microstructure consisting of a silver-rich alpha phase containing some copper, and a copper-rich beta phase containing some silver. Note that the solidus line is horizontal in this region. Such two-phase structures tend to be stronger and more difficult to work.

We also note that at one particular point E on the straight section of the solidus line, at about 28.1% copper, the liquidus and solidus lines touch. This is known as a eutectic point and, like pure metals, eutectic compositions have a melting point, rather than melting range and the lowest melting temperature in the system. The word ‘eutectic’ is from Greek and means ‘easily melted’. Not surprisingly, eutectic alloys are often the basis for solders.

We can also see the composition of sterling silver at 7.5% copper (line X-Y) is just within the solid solubility range of copper in silver only over a small but high temperature range. At lower temperatures, it becomes a two-phase structure, comprising primary alpha phase dendrites and some eutectic mixture of alpha and beta phases.

But most karat golds consist of gold, silver and copper, so the phase diagram becomes more complex. We show it in the form of a prism, with gold, silver and copper represented at the corners of the base triangle, Figure 10. On each face of the prism, we can see the binary phase diagrams that we have just discussed.

We can take horizontal slices through the prism at various temperatures to better see what is happening. Figure 11 is a composite of several slices and shows how the two-phase region of the silver-copper diagram intrudes into the karat golds up to 18K. Thus, depending on composition, 18K, 14K, 10K and 9K gold-silver-copper alloys can be either single phase or two–phase. And remember, we also have the ordered gold-copper phases on the copper side, not shown on this diagram. This is why we water quench such alloys after annealing – to keep them in the single-phase condition which is ductile.

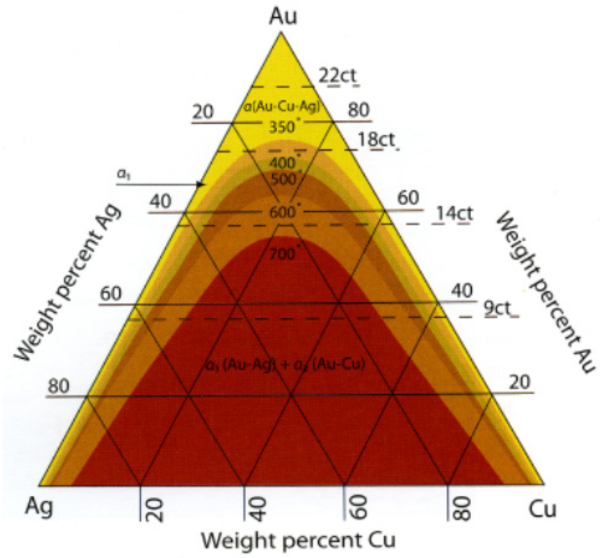


Figure 11: Intrusion of the two-phase region in the gold-silver-copper system as a function of temperature (overlays of horizontal sections of the ternary phase diagram at various temperatures)

If we take vertical slices through our prism at, say, 10K, 14K and 18K, we have what we call pseudo binary phase diagrams, Figure 12. Again, we can see the significant region of immiscibility, leading to two-phase structures at these three karatages.

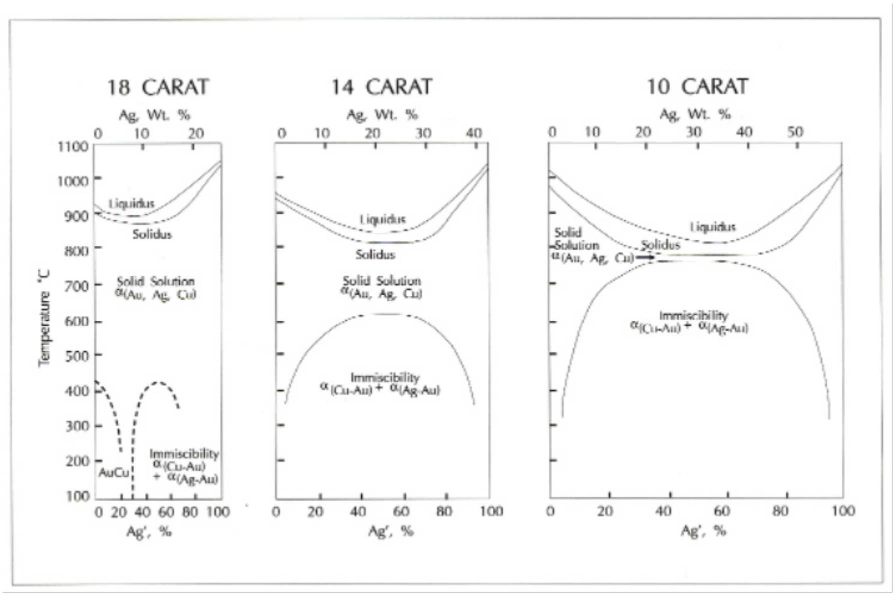
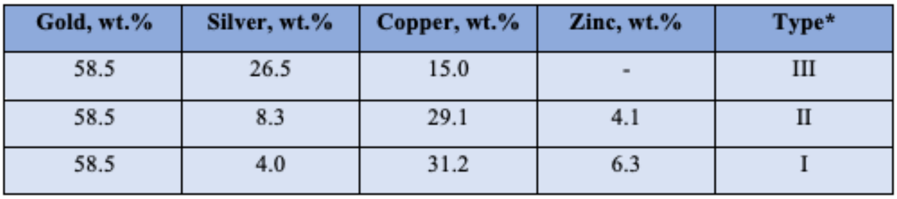


Figure 12: Pseudo-binary phase diagrams for 10K, 14K and 18K gold alloys in the gold-silver-copper system

The amount of second phase, and hence how hard and difficult to work an alloy is, will depend on how close the composition is to the boundary with the single-phase region. Close to it, there will be a little amount. In the center, there will be lots – a 50-50 mixture. McDonald and Sistare,[3] some years ago came up with a system of describing such alloys. Type I alloys are essentially single phase and are easy to work. Type II contain some second phase and are less easy to work and Type III have lots of second phase and are difficult to work. The 14K golds can be particularly difficult to work. So careful selection of alloy composition allows us to obtain golds that are easy to work. But we then restrict ourselves in the colour range that we can get!

Zinc alloying additions tend to contract the region of second phase in karat golds so, if we add some zinc to our alloy, for example, we can free up the alloy in terms of workability, as Table 5 shows. All three 14K gold compositions are the same yellow color, but the zinc additions change the alloy from Type III to Type II and even to Type I.

Table 5: Compositions and Types of Yellow 14K Alloys



Gold, wt.%	Silver, wt.%	Copper, wt.%	Zinc, wt.%	Type*
58.5	26.5	15.0	-	III
58.5	8.3	29.1	4.1	II
58.5	4.0	31.2	6.3	I

** After MacDonald & Sistare[3]: Type 1 – easy to work, Type II – less easy to work, Type III – difficult to work*

White golds: Here in the USA, nickel is used as a primary whitener of gold. However, its metallurgy with gold is difficult, with very limited solubility of nickel in gold, Figure 13. There is a large immiscibility gap –a region of 2 phases - which leads to hard, difficult-to-work alloys. In contrast, palladium is fully soluble in gold-silver alloys and so forms soft ductile alloys.

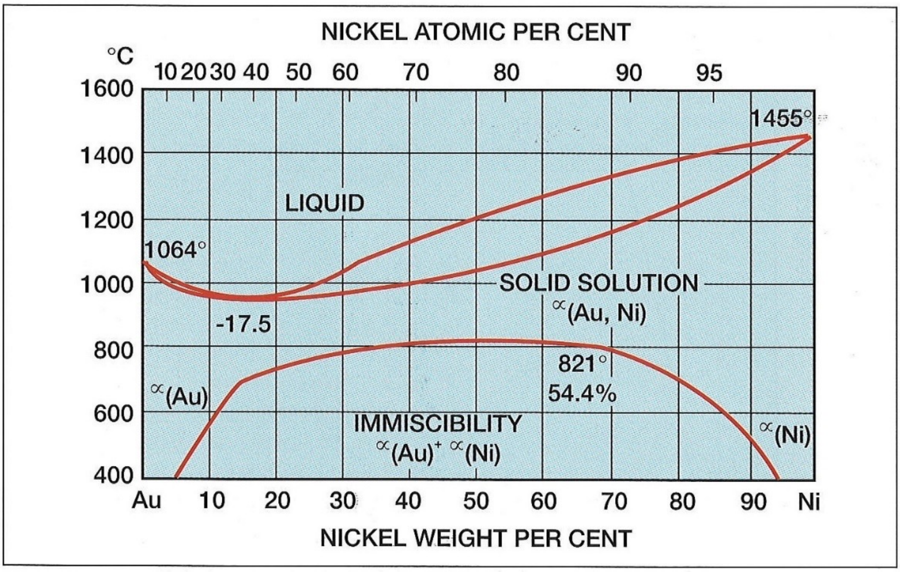


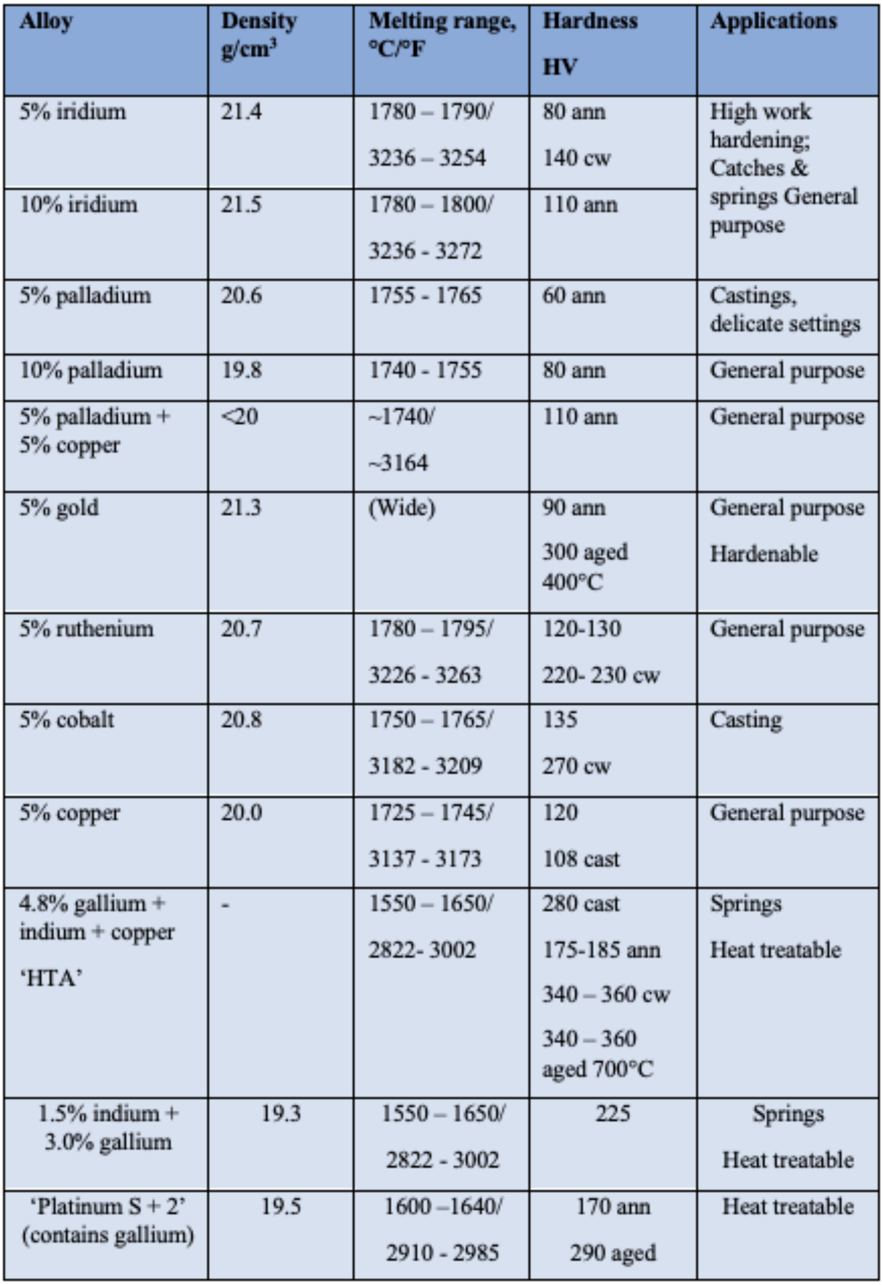
Figure 13: The gold – nickel phase diagram, showing the large area of immiscibility in the solid state

Platinum and palladium alloy phase diagrams: These show similar features to those of gold – limited solid solubility, eutectics, intermetallic/ordered compounds, immiscibility gaps and so on.[4] For platinum, we tend to be interested in 950 and 900 fineness alloys, with 5 and 10% of alloying metals respectively. In this regard, palladium, rhodium and gold have significant solubility, iridium has limited solubility, but for all there are large immiscibility gaps at larger concentrations. In this region of lower finenesses, this results in two phase alloys on cooling to ambient temperatures. Silver has limited solubility in a peritectic system (We have not covered this more complex type of phase diagram), cobalt has good solubility at high temperatures but forms a magnetic intermetallic phase at lower temperatures. As with gold, copper forms an ordered intermetallic compound at low concentrations. This alloying behaviour reflects itself in the common alloys used in jewelry, shown in Table 6.

For palladium, we find similar phase diagrams to those of platinum and gold. Silver is fully soluble at all compositions, gold, copper, rhodium and platinum having significant solubility whilst ruthenium has limited solid solubility. But again, we are mostly interested in 950 fineness alloys which tend to be single phase.

That is all on phase diagrams. We will see some of their uses later. Let’s look at alloying of the precious metals and their effects on microstructure and properties in more detail:

Table 6: Properties of some Common Platinum Alloys

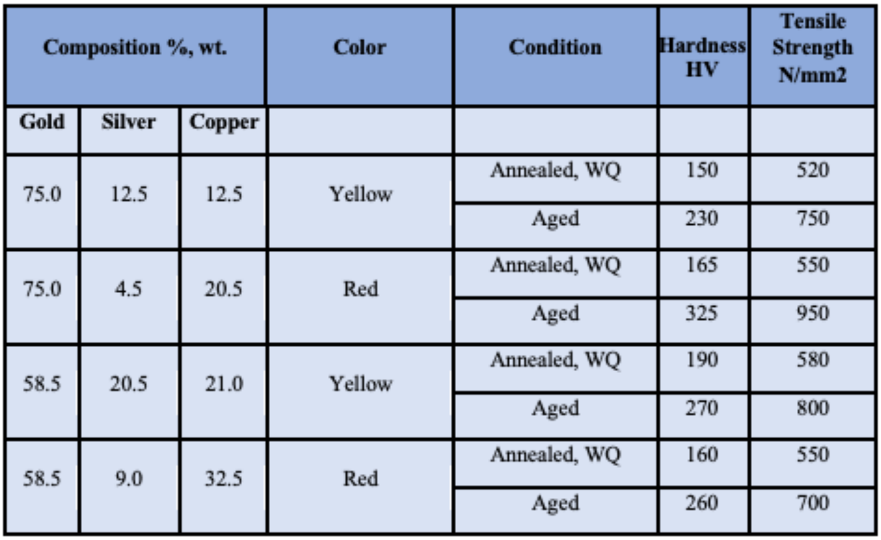


Alloy	Density g/cm^3	Melting range, °C/°F	Hardness HV	Applications
5% iridium	21.4	1780 – 1790/ 3236 – 3254	80 ann 140 cw	High work hardening; Catches & springs General purpose
10% iridium	21.5	1780 – 1800/ 3236 - 3272	110 ann	
5% palladium	20.6	1755 - 1765	60 ann	Castings, delicate settings
10% palladium	19.8	1740 - 1755	80 ann	General purpose
5% palladium + 5% copper	<20	~1740/ ~3164	110 ann	General purpose
5% gold	21.3	(Wide)	90 ann 300 aged 400°C	General purpose Hardenable
5% ruthenium	20.7	1780 – 1795/ 3226 - 3263	120-130 220- 230 cw	General purpose
5% cobalt	20.8	1750 – 1765/ 3182 - 3209	135 270 cw	Casting
5% copper	20.0	1725 – 1745/ 3137 - 3173	120 108 cast	General purpose
4.8% gallium + indium + copper 'HTA'	-	1550 – 1650/ 2822- 3002	280 cast 175-185 ann 340 – 360 cw 340 – 360 aged 700°C	Springs Heat treatable
1.5% indium + 3.0% gallium	19.3	1550 – 1650/ 2822 - 3002	225	Springs Heat treatable
'Platinum S + 2' (contains gallium)	19.5	1600 –1640/ 2910 - 2985	170 ann 290 aged	Heat treatable

HEAT TREATMENT OF KARAT GOLDS TO HARDEN THEM

If we take a water quenched, annealed 18K gold and reheat it at a low temperature (below 400°C/750°F), we can allow the copper-rich second phase to precipitate out in a more controlled manner and get significant hardening of the alloy. We get smaller (and more) precipitates of the second phase within the microstructure, and these are more effective at hardening the alloy. This treatment is known as age-hardening or precipitation-hardening. Typically, we heat at about 280 –300°C/ 535 – 570°F for 3-4 hours. Table 7 shows what we can achieve for 18K and 14K golds. Note for the high copper red 18K gold, we can double the hardness and strength, but the alloy is less ductile.

Table 7: Effect of Heat Treatment on 18K Gold Alloys



Composition %, wt.			Color	Condition	Hardness HV	Tensile Strength N/mm2
Gold	Silver	Copper				
75.0	12.5	12.5	Yellow	Annealed, WQ	150	520
				Aged	230	750
75.0	4.5	20.5	Red	Annealed, WQ	165	550
				Aged	325	950
58.5	20.5	21.0	Yellow	Annealed, WQ	190	580
				Aged	270	800
58.5	9.0	32.5	Red	Annealed, WQ	160	550
				Aged	260	700

18K: annealed 550°C, aged 360°C, 1 h; 14K: annealed 650°C, aged 260°C, 1 h. WQ = water-quenched

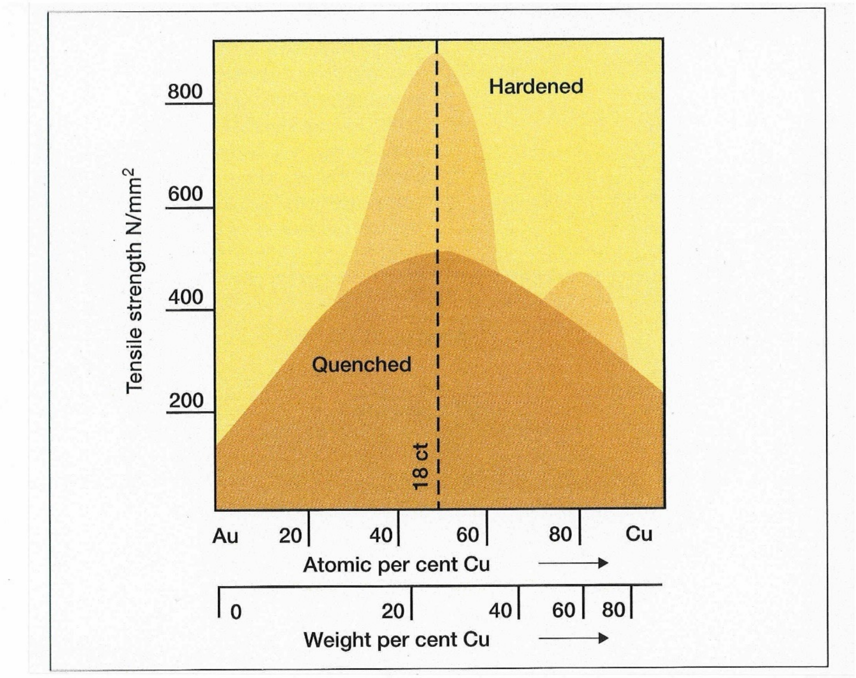


Figure 14: Schematic: Age hardening in gold-copper alloys as a function of composition

Figure 14 shows how the hardness of gold-copper alloys can be increased by age hardening treatments. It centers around 18K alloys with another smaller peak at lower karatages. The time of treatment is important. If we age for too long, we lose some of the strengthening, as shown in Figure 15. This is because the precipitates grow larger (and fewer) by a process called Ostwald ripening and so become less effective at strengthening the alloy.

Such age hardening will help prevent karat gold jewelry from distorting or denting during service and improve wear and scratch resistance. If done before final polishing, it will make polishing easier.

We have seen that alloys with a karatage of 18 and below, and containing copper, can be hardened by a quench and ageing treatment. It is important to remember that, with these alloys, quenching in water from the annealing temperature is necessary to obtain the fully soft condition to allow further working. Then, as a final step before finishing and polishing, the material can be annealed at about 550°C / 1020°F, quenched, then aged at 280°C / 535°F to give an increase in strength.

Heat treatment of silver and platinum: Similar hardening can be obtained in conventional sterling silver, as reported by Grimwade,[1] but note that soldering hinders use of this benefit. However, some newer silver alloys with improved tarnish and firestain resistance can be age-hardened. Most 950 platinum alloys are not amenable to age hardening treatment, but some heat treatable alloys have been developed.[5,6] These are based on alloys containing indium and/or gallium and hardnesses of up to HV360 can be obtained. All such alloys harden by precipitating out a second phase as small particles distributed evenly in the microstructure.

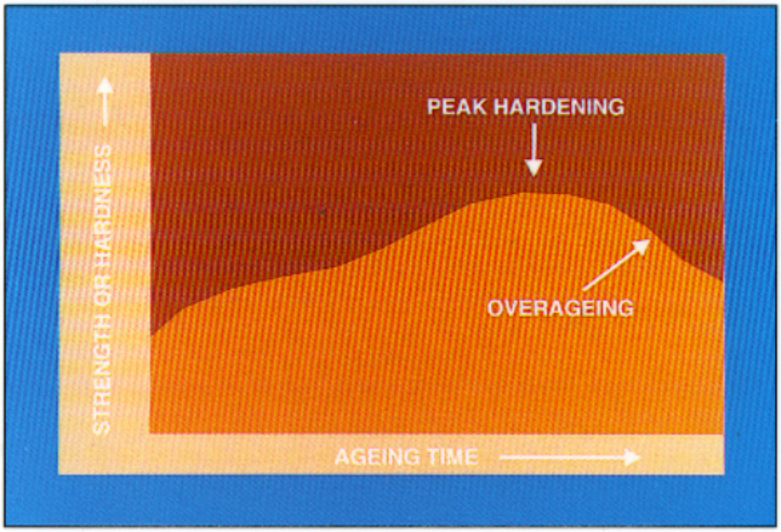


Figure 15: Schematic: Effect of ageing time on hardness during ageing heat treatment. Note the drop in hardness if overage beyond optimum time.

Earlier, I mentioned that we often add small alloying additions to the colored karat golds to control properties. Let us look at this aspect now.

ALLOY ADDITIONS TO KARAT GOLDS

Apart from silver and copper, other additions may be made to karat golds to enhance properties, often tailored to particular applications, e.g. for stamping golds or casting golds. These include zinc, silicon and grain refiners. Of these, zinc is probably the most common.

Zinc: Zinc is added in small amounts, typically 0.5%, as a deoxidiser to give clean melts and additions of up to 2% can provide improved melt fluidity and enhanced mold filling in investment (or lost wax) casting. Larger amounts, up to 10%, are added to improve the workability of 8 - 14K golds, making them more suitable for stamping operations, for example. This is because of its influence on the phase diagram, discussed earlier. Zinc also lowers the melting range, and so additions must be limited to avoid subsequent difficulties in soldering. For this reason, zinc is a major addition in karat gold solders, along with other low melting point metals such as tin, indium (and formerly cadmium). If large additions of zinc are made, the copper content is usually also increased at the expense of silver to maintain color. Zinc, like silver, tends to whiten golds.

Zinc is very volatile and evaporates easily from molten gold alloys. To minimize zinc loss, we add zinc, wrapped in copper, silver or gold sheet, at the last minute, plunging it under the melt surface, or we add it as a copper-zinc alloy – i.e. brass. Make sure it is not a lead-containing free-machining brass or we may end up embrittling our alloy!

Silicon: Very small additions of silicon, added as a copper-silicon master alloy, find use as a deoxidiser in investment casting alloys up to 18K. It gives cleaner, brighter castings. However, the quantity added must be strictly controlled at levels well below 0.05% at 18K to avoid embrittlement.[7] The amount of silicon that can be tolerated before embrittlement occurs increases as karatage is lowered below 18K. Never use silicon in high karat golds. The expert advice is to only consider use of silicon in alloys bought from the specialist alloy producers.

A problem that can arise in the use of silicon in investment casting alloys is the formation of cracks in the casting after quenching the flask.[8] It can also result in large grain (crystal) sizes. So, use it carefully. One major producer of 14K jewelry stopped use of silicon in preference to use of a grain refined gold, with improved casting yields.[9]

Grain Refiners: Very small additions of grain refiners, typically at levels of about 0.1% or less, may also be added to karat golds to promote a fine (small) grain size in the alloy. They include iridium, ruthenium and cobalt. Iridium and ruthenium are effective in casting, where they promote nucleation of crystals during solidification, and cobalt is effective during annealing of cold worked material, where it promotes nucleation of grains during recrystallization. Figure 16 shows the fine grain structure of an annealed 18K gold with iridium additions, compared to that without iridium. If too much is added or it is not well dispersed, one can get nests of hard iridium particles at the surface that give rise to 'comet tailing' defects on polishing, as Faccenda has described.[10] Note that grain refiners are not effective in silicon-containing alloys.

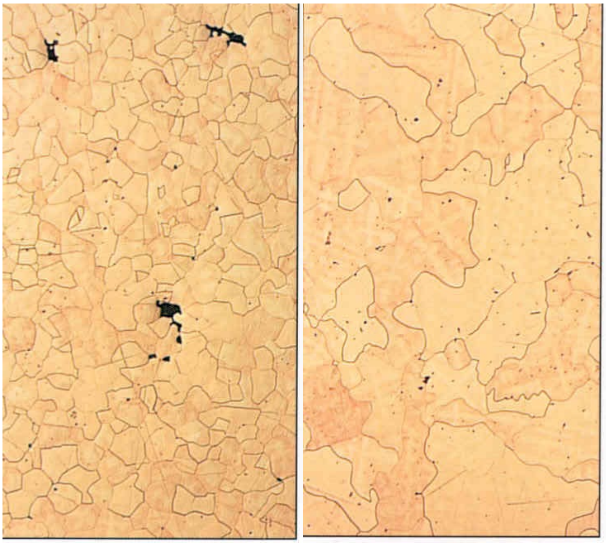


Figure 16: Grain refining by Iridium additions in 18K gold (left - with 0.005% Ir, right – without Ir)

The amount of cobalt that can be added is also sensitive to copper content of the alloy, as Ott has shown.[11] Its effect in grain refining a 14K gold is shown in Figure 17.

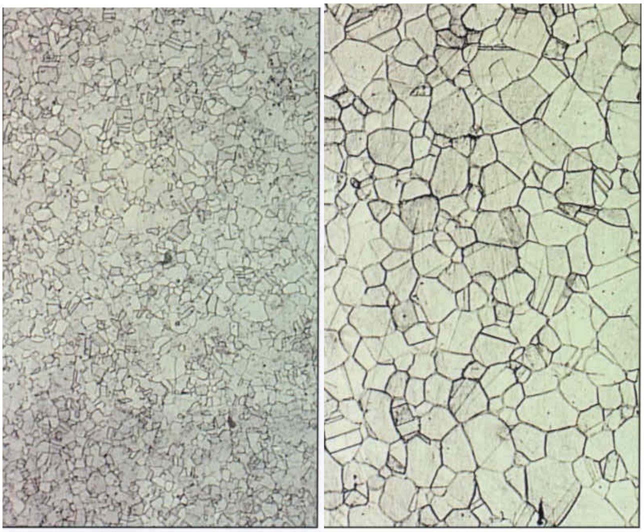


Figure 17: Grain refining of soft annealed 14K gold by cobalt additions (left – with Co, right – without Co)

Impurities: Many impurities, that can find their way into jewelry alloys via contaminated scraps or during melting, can segregate to grain boundaries and cause embrittlement at very low concentrations in all precious metal jewelry alloys. These include lead, silicon, sulfur, tin, selenium, bismuth and other low melting metals, as Ott has discussed11. Many form low melting point compounds or eutectics with the parent metal. Examples of such embrittlement in karat golds can be found in the Defects Handbook,[12] but silver, platinum and palladium are also similarly susceptible.

For completeness, we should also mention gaseous impurities, particularly oxygen but also hydrogen. These dissolve easily in molten alloys but can precipitate out on solidification or annealing, causing gas porosity in castings and blistering in wrought sheet. Silver is well known to suffer from such problems, but all jewelry metals are susceptible. Gas porosity can also develop in investment casting due to reaction with the investment mold surface on casting,[12] when sulfur dioxide gas is formed that dissolves in the surface of the molten metal and precipitates out as gas pores on solidification.

WHITE KARAT GOLD ALLOYS

White golds for jewelry were originally developed as a substitute for platinum and are particularly popular currently in the West. Apart from gold and copper, all pure metals are white or gray and their addition to gold will tend to bleach or lighten its color. In practice, palladium and nickel are strong bleachers of gold, silver and zinc are moderate bleachers while other metals have a moderate to weak effect. This has given rise to two classes of commercial white golds - the nickel white and the palladium white golds, although at the 9/10 karat level it is possible to produce a reasonable white gold by the addition of silver alone, as mentioned earlier. Note there is a limit in karatage range for white golds up to 21K.

Nickel whites: As mentioned earlier, nickel alloying additions form hard and strong white golds up to 18K. They are difficult to work because gold and nickel form a massive region of two phases, Figure 13. So, many commercial alloys tend to be low in nickel content and also contain silver and zinc to obtain whiteness, often with an addition of copper to improve workability. The low nickel and the copper result in a yellowish-brown tint to the white color.

Consequently, such poor white color golds are often rhodium plated to give a good, tarnish-resistant white color that should last for some years before the coating wears away. Unfortunately, many people are allergic to nickel and can develop a skin rash when wearing nickel-white gold. In Europe, legislation has been introduced to restrict the use of nickel[13,14] and in Europe these nickel-rich alloys are now phased out. That said, many commercial alloys contain some nickel (typically 2-4%, and no more than 6%), but below the metal release limits demanded by the legislation.

Palladium whites: Additions of 10 to 12% of palladium to gold impart a good white color, but palladium is an expensive metal and denser than nickel. Thus, palladium white golds are more expensive than nickel-white golds because of the cost of the palladium and their higher density: the pieces are heavier and so contain more gold. In addition, the high melting point of palladium means that these golds are more difficult to melt. However, the alloys are considerably softer and easier to work than the nickel golds. They are useful for gem setting purposes. They are available in karatages up to 21K (gold-12.5% palladium).

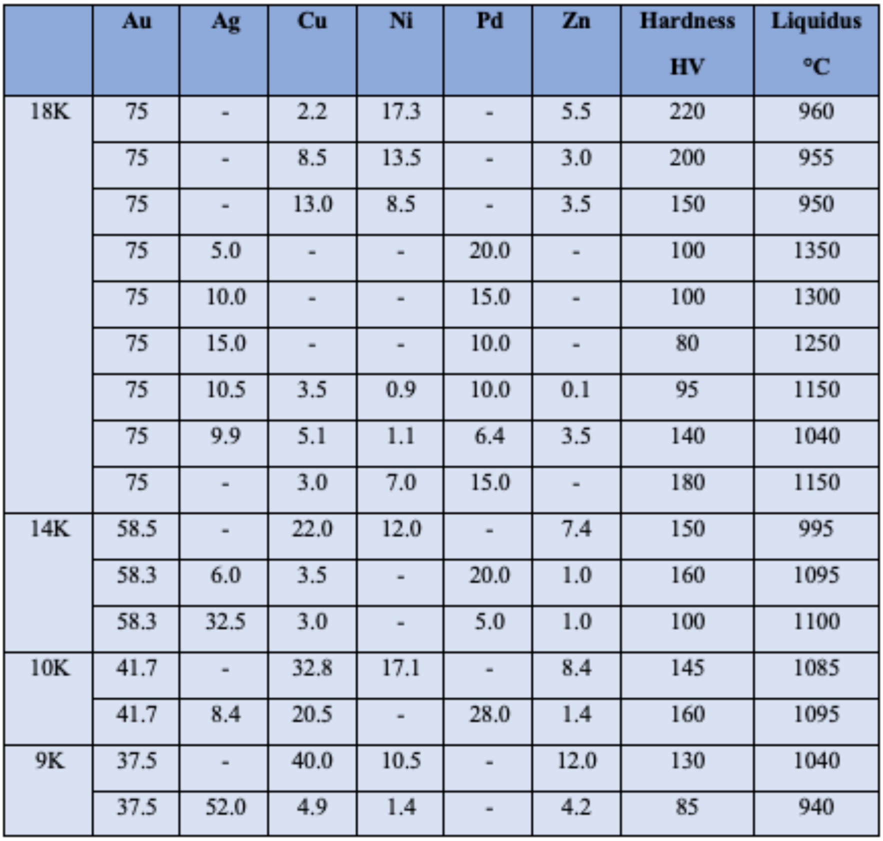
Many commercial palladium white golds contain only about 6 to 8% palladium with additions of silver, zinc and copper, and even some nickel, in an attempt to keep the cost down. These alloys have a less satisfactory white colour and will often be rhodium-plated.

Table 8 shows some typical white golds and their properties, illustrating the higher hardness of the nickel whites and the higher melting temperatures of the palladium whites. With the high cost of palladium, alternative white golds have been developed. These often contain manganese and other metals such as iron and chromium.[21] However, many are difficult to work and cast, tend to crack and tarnish and may also require rhodium plating due to their poor white colour. More recently, the use of gallium[15] and germanium[16] have been explored as primary whiteners.

It is not possible to make a 22K white gold because the available 8.4% of alloy addition is not sufficient to give a good white colour.

Commercial white golds can vary significantly in their degree of whiteness and there was no agreed definition of what constitutes ‘white’. This problem has been addressed by an industry-led working party under the auspices of the MJSA and World Gold Council in 2003 and there is now an agreed definition in terms of the parameter, the Yellowness Index and a white gold is defined as having a YI=35 or less. Within this definition, three grades of whiteness are accepted.[17]

Table 8: Typical White Gold Alloys



	Au	Ag	Cu	Ni	Pd	Zn	Hardness HV	Liquidus °C
18K	75	-	2.2	17.3	-	5.5	220	960
	75	-	8.5	13.5	-	3.0	200	955
	75	-	13.0	8.5	-	3.5	150	950
	75	5.0	-	-	20.0	-	100	1350
	75	10.0	-	-	15.0	-	100	1300
	75	15.0	-	-	10.0	-	80	1250
	75	10.5	3.5	0.9	10.0	0.1	95	1150
	75	9.9	5.1	1.1	6.4	3.5	140	1040
	75	-	3.0	7.0	15.0	-	180	1150
14K	58.5	-	22.0	12.0	-	7.4	150	995
	58.3	6.0	3.5	-	20.0	1.0	160	1095
	58.3	32.5	3.0	-	5.0	1.0	100	1100
10K	41.7	-	32.8	17.1	-	8.4	145	1085
	41.7	8.4	20.5	-	28.0	1.4	160	1095
9K	37.5	-	40.0	10.5	-	12.0	130	1040
	37.5	52.0	4.9	1.4	-	4.2	85	940

Au – gold; Pd- palladium; Ag- silver; Cu - copper; Zn - zinc, Ni - nickel. [In wt. %]

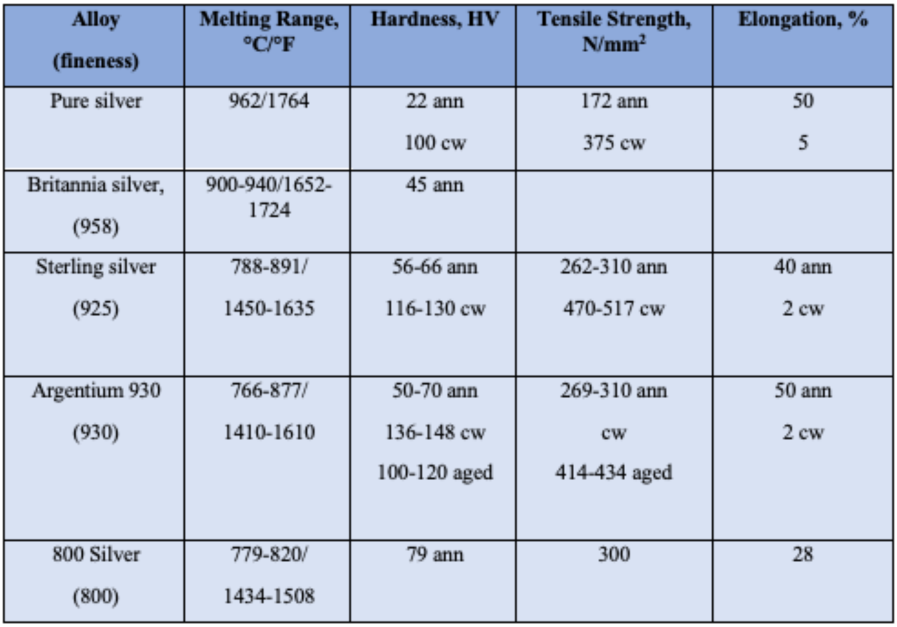
SILVER ALLOYS

Table 9 shows some properties of various silver alloys including conventional sterling silver, 92.5% silver – 7.5% copper. This alloy is very malleable with reasonable properties, although it does suffer from firestain and a tendency to tarnish. Copper is a much smaller atom than silver and hence is an effective hardener, as it is with karat golds. Where a more ductile alloy is required (e.g. for spinning and chain-making), zinc can replace some of the copper in sterling silver. It also acts as a deoxidiser and improves fluidity in investment casting.[21] Use of zinc in such alloys confers a whiter color.

We have already seen the silver-copper phase diagram, Figure 9, and know that some strengthening by heat treatment is possible. Here, the material is solution- annealed at around 750°C/ 1380°F (to maximise the amount of copper in solid solution), above the normal annealing temperature, and water quenched before aging for about 1 hour at 300°C/570°F. This precipitates the copper-rich beta phase as very fine particles within the matrix silver-rich alpha phase. The problem is that where items have been silver soldered, the high solution-treatment temperature is above the soldering temperature with obvious consequences. Soldering after heat treatment does not get around the problem either, as the soldering temperature causes overaging and loss of the age hardening. Fischer-Buehner18 has discussed hardening of sterling silver and grain refinement in his Santa Fe Symposium paper presented in 2003. A harder, stronger sterling silver that is age-hardenable has recently been developed by Stuller[19,20] and is an Ag-Cu-Pd-Sn-Zn composition containing about 2.75% Pd.

Britannia silver is an alloy of 95.8% silver- copper and is consequently not as hard as sterling silver and so finds little use today. Lower finenesses of silver such as 800 (80% silver – 20% copper plus zinc) or 830 grades find application in some countries, and these have higher hardness and strength but lower ductility as a consequence of the higher proportion of eutectic phases in the alloy. The higher copper content also imparts a more yellow color, and such alloys are often electroplated with silver to improve the color.

Table 9: Properties of Some Silver Alloys



Alloy (fineness)	Melting Range, °C/°F	Hardness, HV	Tensile Strength, N/mm²	Elongation, %
Pure silver	962/1764	22 ann 100 cw	172 ann 375 cw	50 5
Britannia silver, (958)	900-940/1652-1724	45 ann		
Sterling silver (925)	788-891/ 1450-1635	56-66 ann 116-130 cw	262-310 ann 470-517 cw	40 ann 2 cw
Argentium 930 (930)	766-877/ 1410-1610	50-70 ann 136-148 cw 100-120 aged	269-310 ann cw 414-434 aged	50 ann 2 cw
800 Silver (800)	779-820/ 1434-1508	79 ann	300	28

ann = annealed, cw = cold-worked

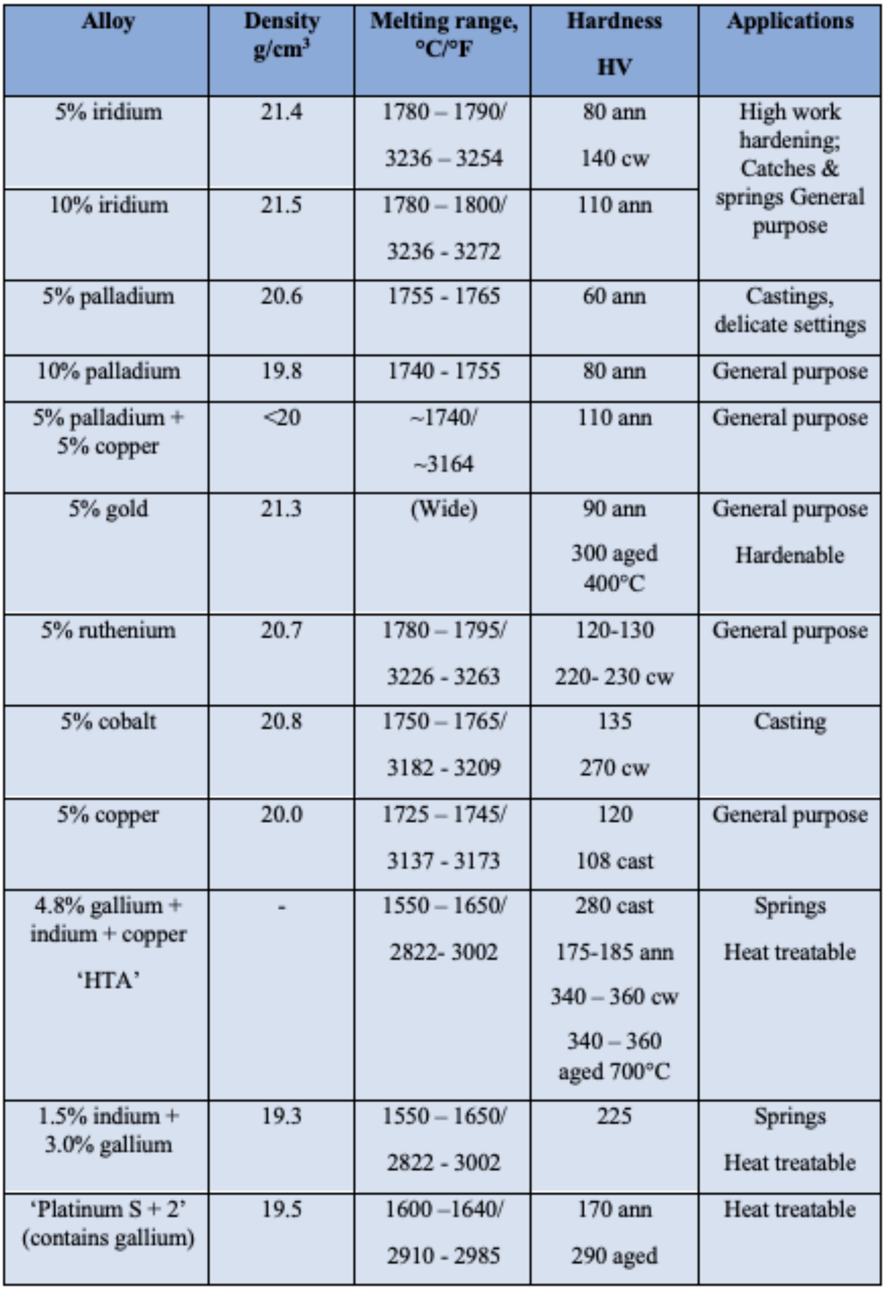
Tarnish resistance: There are a number of so-called ‘tarnish resistant’ silvers on the market in both the USA and Europe; some have been discussed earlier at Santa Fe Symposia,[21-24] and the causes of tarnishing have been discussed by Basso.[25] These are based on alloying with elements that preferably form a transparent oxide on the surface that hinders formation of silver-copper sulphides, which is the cause of the black tarnish. Typically, these are metals such as germanium or indium or silicon or even some gold or platinum group metals such as platinum or palladium. Hardening by heat treatment (i.e. age hardening) is possible in some of these; in the Argentium™ alloy,[23] some of the copper is substituted by more than 1% germanium. Some copper is desirable, as hardening is achieved by precipitates of Cu_3Ge phase in the silver-rich matrix grains.

Firestain: As Grimwade and others have discussed,[21,26,27] firestain is caused by internal oxidation of the copper in sterling silver. Many of the tarnish-resistant silvers also claim to reduce or eliminate firestain (but this is not necessarily true, as borne out by metallographic examination of cross-sections[29] of annealed material; other alloying metals such as zinc can form sub-surface oxides. Even though the surface may not appear darkened, subsequent polishing will reveal it sub-surface). The obvious answer to this problem is to eliminate copper altogether. However, use of alloying additions such as zinc and tin do not result in alloys of sufficient hardness compared to sterling silver and they are not hardenable by heat treatment. One such alloy in the UK, based on silver-zinc-tin-indium only has an annealed hardness of HV45.[28]

PLATINUM ALLOYS

Compared to the karat golds, platinum jewelry alloys are generally of high fineness, typically 900 and 950 (although there are lower finenesses such as 585 being promoted) and, with alloying contents of only 5 or 10%, are metallurgically more straightforward, as Battaini has demonstrated.[29] Most are single phase solid solution alloys, although some can be age hardened.

Table 10: Properties of Some Common Platinum Alloys

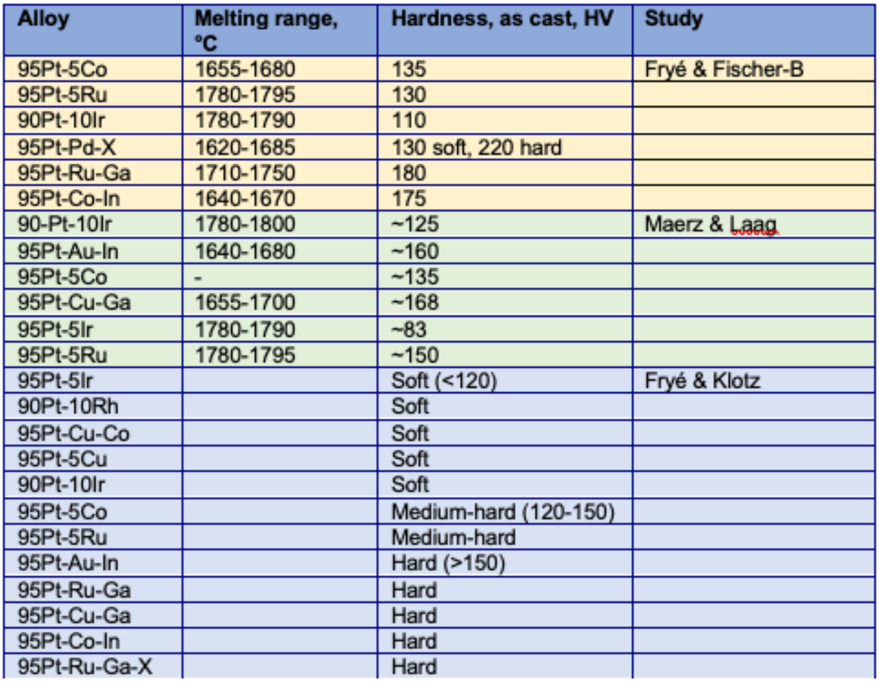


Alloy	Density g/cm³	Melting range, °C/°F	Hardness HV	Applications
5% iridium	21.4	1780 – 1790/ 3236 – 3254	80 ann 140 cw	High work hardening; Catches & springs General purpose
10% iridium	21.5	1780 – 1800/ 3236 - 3272	110 ann	
5% palladium	20.6	1755 - 1765	60 ann	Castings, delicate settings
10% palladium	19.8	1740 - 1755	80 ann	General purpose
5% palladium + 5% copper	<20	~1740/ ~3164	110 ann	General purpose
5% gold	21.3	(Wide)	90 ann 300 aged 400°C	General purpose Hardenable
5% ruthenium	20.7	1780 – 1795/ 3226 - 3263	120-130 220- 230 cw	General purpose
5% cobalt	20.8	1750 – 1765/ 3182 - 3209	135 270 cw	Casting
5% copper	20.0	1725 – 1745/ 3137 - 3173	120 108 cast	General purpose
4.8% gallium + indium + copper 'HTA'	-	1550 – 1650/ 2822- 3002	280 cast 175-185 ann 340 – 360 cw 340 – 360 aged 700°C	Springs Heat treatable
1.5% indium + 3.0% gallium	19.3	1550 – 1650/ 2822 - 3002	225	Springs Heat treatable
'Platinum S + 2' (contains gallium)	19.5	1600 –1640/ 2910 - 2985	170 ann 290 aged	Heat treatable

Table 10 shows properties of common alloys used worldwide. As can be seen, density does not vary greatly, whereas melting range does. Some alloys such as the 5% palladium alloy are quite soft whilst others are quite hard. The 5% cobalt alloy is considered the best casting alloy, which is, perhaps, related to its narrow melting range. Its moderately high hardness reflects the fact that it is barely a two-phase alloy with some $CoPt_3$ as the hardening phase. Color does not vary much with alloy composition. The hardenable alloys contain gallium, which has a limited solid solubility in platinum of about 6% maximum, which drops to around 2.5% at lower temperatures. This enables precipitation hardening by the Pt_3Ga phase on heat treatment, as Normandeau has discussed,[30] in a similar way to that discussed earlier for sterling silver.

Another advantage of adding low melting point additions such as gallium and indium is that they lower the melting temperatures and this is advantageous when investment casting, as has recently been discussed.[31] This has led to a number of new alloys being developed[31] with such additions, as shown in Table 11, with significantly reduced melting temperatures.

Table 11: Range of Platinum Alloys Studied in Casting Trials Since 2000



Alloy	Melting range, °C	Hardness, as cast, HV	Study
95Pt-5Co	1655-1680	135	Fryé & Fischer-B
95Pt-5Ru	1780-1795	130	
90Pt-10Ir	1780-1790	110	
95Pt-Pd-X	1620-1685	130 soft, 220 hard	
95Pt-Ru-Ga	1710-1750	180	
95Pt-Co-In	1640-1670	175	
90-Pt-10Ir	1780-1800	~125	Maerz & Laag
95Pt-Au-In	1640-1680	~160	
95Pt-5Co	-	~135	
95Pt-Cu-Ga	1655-1700	~168	
95Pt-5Ir	1780-1790	~83	
95Pt-5Ru	1780-1795	~150	
95Pt-5Ir		Soft (<120)	Fryé & Klotz
90Pt-10Rh		Soft	
95Pt-Cu-Co		Soft	
95Pt-5Cu		Soft	
90Pt-10Ir		Soft	
95Pt-5Co		Medium-hard (120-150)	
95Pt-5Ru		Medium-hard	
95Pt-Au-In		Hard (>150)	
95Pt-Ru-Ga		Hard	
95Pt-Cu-Ga		Hard	
95Pt-Co-In		Hard	
95Pt-Ru-Ga-X		Hard	

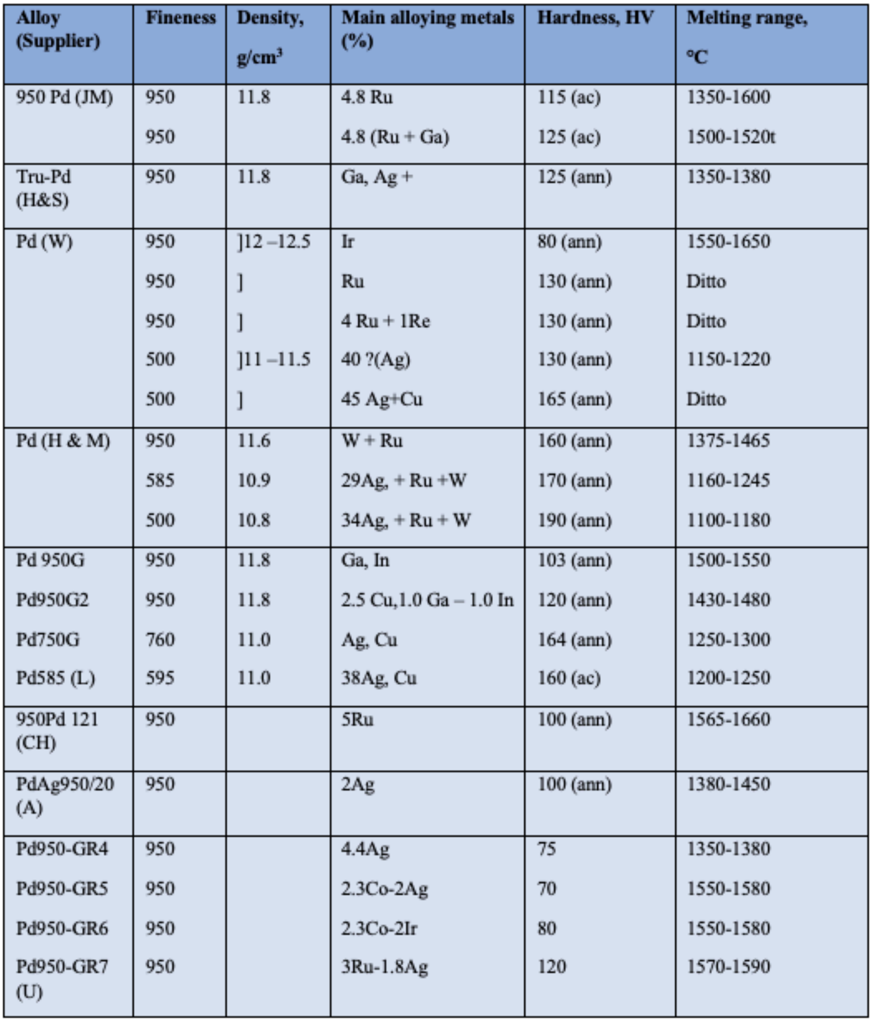
X - additional elements unknown at time of publication (from reference 31)

PALLADIUM ALLOYS

There is comparatively little information on the metallurgy and compositions of the new 950 palladium alloys appearing on the market. Many are based on palladium-ruthenium, with other additions, including silver. Table 12 shows some typical commercial alloys. Ruthenium has a very limited solubility in palladium,[4] so such alloys can be expected to be two-phase in structure. Hardness values mirror the equivalent platinum alloys, Table 10. On the other hand, the melting temperatures of the 950 alloys tend to much lower. In Europe, there are lower fineness alloys at 585 and 500 on the market, with slightly higher hardnesses compared to the 950 alloys and with lower densities and melting ranges.

Battaini has recently discussed development of 950 palladium-copper- and palladium-gallium- based alloys;[32] the gallium alloy showed most promise. This alloy contains 3.5% gallium, which is at the limit of solid solubility, with small additions of copper, indium and aluminum too. It has an annealed hardness of HV 70, rising to HV310 after 70% cold work. It is assumed that this is basically a single-phase alloy.

Table 12: Typical Palladium Alloys

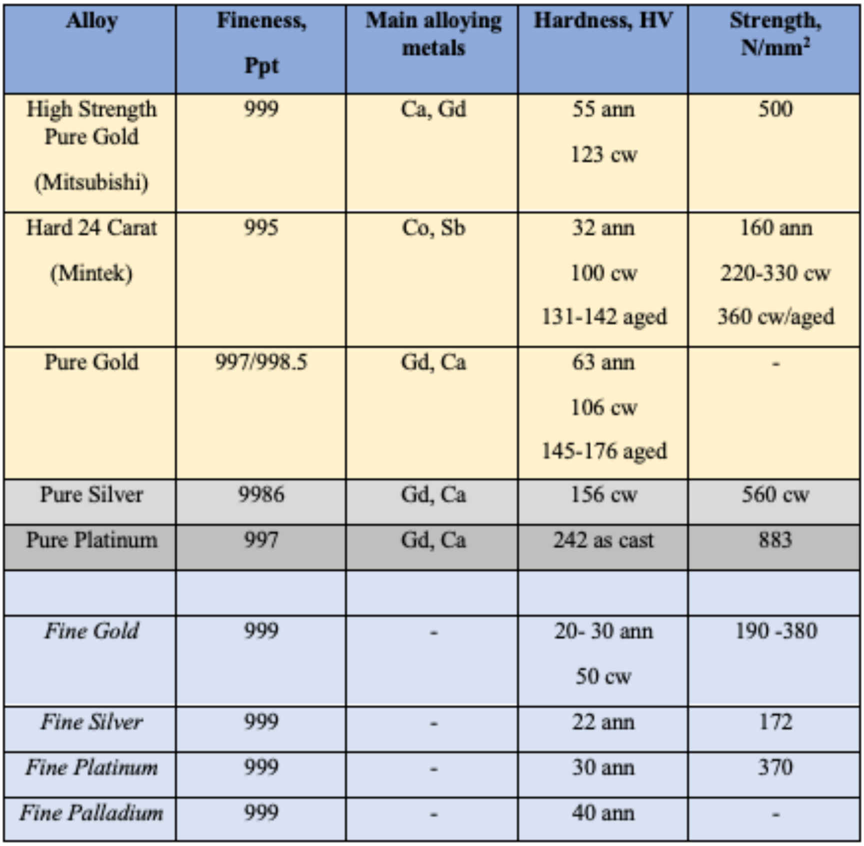


Alloy (Supplier)	Fineness	Density, g/cm^3	Main alloying metals (%)	Hardness, HV	Melting range, °C
950 Pd (JM)	950	11.8	4.8 Ru	115 (ac)	1350-1600
	950		4.8 (Ru + Ga)	125 (ac)	1500-1520t
Tru-Pd (H&S)	950	11.8	Ga, Ag +	125 (ann)	1350-1380
Pd (W)	950	]12 –12.5	Ir	80 (ann)	1550-1650
	950	]	Ru	130 (ann)	Ditto
	950	]	4 Ru + 1Re	130 (ann)	Ditto
	500	]11 –11.5	40 ?(Ag)	130 (ann)	1150-1220
	500	]	45 Ag+Cu	165 (ann)	Ditto
Pd (H & M)	950	11.6	W + Ru	160 (ann)	1375-1465
	585	10.9	29Ag, + Ru +W	170 (ann)	1160-1245
	500	10.8	34Ag, + Ru + W	190 (ann)	1100-1180
Pd 950G	950	11.8	Ga, In	103 (ann)	1500-1550
Pd950G2	950	11.8	2.5 Cu,1.0 Ga – 1.0 In	120 (ann)	1430-1480
Pd750G	760	11.0	Ag, Cu	164 (ann)	1250-1300
Pd585 (L)	595	11.0	38Ag, Cu	160 (ac)	1200-1250
950Pd 121 (CH)	950		5Ru	100 (ann)	1565-1660
PdAg950/20 (A)	950		2Ag	100 (ann)	1380-1450
Pd950-GR4	950		4.4Ag	75	1350-1380
Pd950-GR5	950		2.3Co-2Ag	70	1550-1580
Pd950-GR6	950		2.3Co-2Ir	80	1550-1580
Pd950-GR7 (U)	950		3Ru-1.8Ag	120	1570-1590

ann = annealed; ac = as cast

JM – Johnson Matthey Plc; H&S – Hoover & Strong Inc; W – Wieland GmbH; H & M – Heimerle & Meule GmbH; L – Legor Srl; CH – C Hafner; A – Agosi; U – United; Data taken from manufacturer's literature.

Table 13: Typical Properties of Microalloys (versus the pure metals)



Alloy	Fineness, Ppt	Main alloying metals	Hardness, HV	Strength, N/mm^2
High Strength Pure Gold (Mitsubishi)	999	Ca, Gd	55 ann 123 cw	500
Hard 24 Carat (Mintek)	995	Co, Sb	32 ann 100 cw 131-142 aged	160 ann 220-330 cw 360 cw/aged
Pure Gold	997/998.5	Gd, Ca	63 ann 106 cw 145-176 aged	-
Pure Silver	9986	Gd, Ca	156 cw	560 cw
Pure Platinum	997	Gd, Ca	242 as cast	883
Fine Gold	999	-	20- 30 ann 50 cw	190 -380
Fine Silver	999	-	22 ann	172
Fine Platinum	999	-	30 ann	370
Fine Palladium	999	-	40 ann	-

ann = annealed; cw = cold-worked

MICROALLOYS

There are a number of 24K gold and platinum alloys on the market that show high hardness and strength even though they only contain very small alloying additions such as calcium and the rare earth metals (usually gadolinium), at levels of less than 0.5%, typically 0.3%. Microalloys in silver and palladium are also possible. The basis of their metallurgy has been described in previous papers.[33-36]

In such alloys the alloying metals are only slightly soluble in the precious metal and form high precious metal-content, hard second phases of intermetallic compounds in the microstructure, which confer considerable precipitation hardening in exactly the same way as described earlier. Some of the microalloys can be heat treated to optimize hardness and strength. Table 13 shows typical properties that can be achieved in such alloys. For the microalloyed golds, hardness values approaching those of 18K golds can be achieved.

SOLDERS

The metallurgy of solders is the same as the jewelry alloys discussed earlier. Two of the most important requirements are low melting temperatures and good melt fluidity. Color is also important for the karat golds since it need to match that of the parent metals being joined. For golds and silver particularly, solders are based on the jewelry alloy compositions with heavier additions of low melting metals such as zinc, indium and tin in order to lower the melting temperature as well as conferring good melt fluidity. Cadmium is technically a good addition to solders but, unfortunately, it is very volatile and forms an oxide that is highly toxic. This has resulted in a ban on its use in many countries. The toxicity problems of cadmium and its effects on the health of the workforce have been well documented in the early Santa Fe Symposia. For platinum and palladium, there is usually more flexibility and, although platinum- and palladium-based solders are available, other compositions such as white gold solders may be used.

CONCLUSIONS

This has been a rapid review of the basic nature of metals and alloys, followed by an examination of the effects of alloying on the properties of the principal precious metals used in jewelry. We commenced with a discussion of some of the properties of the colored karat gold alloys and what one can deduce. We have examined phase diagrams and how one can interpret and use them. Finally, we have looked at the other precious metals and how alloying affects properties.

I have attempted to show how the properties of precious metal jewelry alloys are derived from their composition, but we should also note that their microstructure and processing history, i.e. their metallurgy, is also important. All are interrelated and influence both their ‘manufacturability’ and performance in service as jewelry. Importantly, we can tune the properties by careful choice of alloying additions to suit manufacturing needs. Understanding of the metallurgy of jewelry alloys enables the jeweler to optimize his or her choice of alloy and processing route and the final properties of the finished piece without risk of cracking or other defect formation or poor performance in service. In the next part, we will examine microstructure and how it is affected by casting, deformation and annealing.

This presentation can only be regarded as an introduction to the metallurgy of the precious metals, but I hope it will help you to understand a little bit more about the materials you work with. Perhaps it will help you to solve or even avoid some of the problems goldsmiths and jewelers often face and encourage you to seek the advice, guidance and further knowledge that will take our industry forward.

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