Chris Corti
COReGOLD Technology,
Reading, UK

Dr Chris Corti is a technologist with over 38yrs experience developing and exploiting technology in the precious metals industry. He worked with Johnson Matthey Plc and World Gold Council before setting up his own technology consultancy in 2009. He studied metallurgy at University and has worked in the energy industry in the UK and Switzerland before moving into the precious metal industry. He has published widely and presented on jewellery topics many times at the Jewellery Technology Forum and the Santa Fe Symposium.

Heat treatment of precious metal jewellery alloys is often referred to in the literature but many practitioners do not have a clear understanding of what this term means and its importance to the jewellery industry. It is a term often used by metallurgists to describe a range of thermal processes designed to manipulate properties of engineering and decorative alloys to meet requirements. Many will be familiar with heating and quenching of steel to harden it, whilst age-hardening of steels and aluminium alloys is an example of a two-stage treatment that is widely used to confer additional strength.

Many treatments involve heating of the alloys to specific temperatures for specified periods of time and then cooling at a defined rate that may be rapid or slow. In jewellery, annealing of precious metal alloys is often undertaken to soften cold-worked material to enable further working without cracking or fracture. But other types of annealing are also carried out, for example to stress relieve alloy items to prevent stress corrosion cracking or to age-harden them. In investment casting, the burning out of casting moulds ('flasks') requires a defined temperature and time cycle to enable good castings to be achieved. This is also an example of a heat treatment.

Whilst annealing and age-hardening of jewellery metals has been featured in previous JTF presentations, the 'whys' and 'wherefores' of such treatments have not, perhaps, been fully explained. There are several types of annealing treatments in use, each with different objectives. This presentation focuses on heat treatments used in the jewellery industry and attempts to explain the underlying principles involved. Examples of heat treatments of base metal alloys are also included to demonstrate that such treatments are universal.

"Improving the Properties of Precious Metals by Heat Treatment"

Chris Corti
COReGOLD Technology,
Reading, UK

INTRODUCTION

A participant at a recent jewellery technology symposium made a remark, following my Basic Metallurgy presentation[1], "I don't understand what 'heat treatment' is!". It made me think whether I have missed something important in this series of presentations made at the Santa Fe Symposia. Actually, it is mostly covered but, perhaps, was not fully clear and explained as a discrete topic. This presentation is made to repair this omission.

So what does the term 'Heat treatment' mean and what does it cover? Basically, it is a broad term to cover any treatment of a metal or alloy that involves heating it for a period of time to change some aspect of its properties. To put it more technically, heat treatment is a term often used by metallurgists to describe a range of thermal processes designed to manipulate properties of engineering and decorative alloys to meet requirements. Heating and quenching of steel to harden it is one example that results from a phase change from austenite to martensite, a phase change that involves the shearing of atoms within the crystals (grains). The crystal structure changes from face-centered cubic (FCC) to face-centered tetragonal (FCT). Age-hardening (or precipitation hardening) of steels and aluminum alloys are examples of a two-stage treatment that is widely used to confer additional strength, often at the expense of some ductility. Hardening of die steels for forging and stamping operations is one example with which many of us will be familiar. We can use this mechanism for some jewellery alloys too, as we shall see later.

Many treatments involve heating of the alloys to specific temperatures for specified periods of time and then cooling at a defined rate that may be rapid or slow. In jewellery, annealing of precious metal alloys is often undertaken to soften cold-worked material to enable further working without cracking or fracture. But other types of annealing are also carried out: for example, to stress relieve alloy items to prevent stress corrosion cracking or to age-harden them. To cite a non-metallic example: in investment casting, the burning out of casting molds ('flasks') requires a defined temperature and time cycle to enable good quality moulds (and hence castings) to be achieved. This is also a heat treatment of the mould!

Whilst annealing and age-hardening of jewellery metals has been discussed in previous 'Basic Metallurgy' presentations, the 'whys' and 'wherefores' of such treatments have not, perhaps, been fully explained. There are several types of annealing treatments in use, for example, each with different objectives. This presentation focuses on heat treatments used in the jewellery industry and attempts to explain the underlying principles involved. I will also give some other examples for base metal alloys used in the engineering industries.

TYPES OF HEAT TREATMENT

There are many types of heat treatment in use in the metallurgical industry. Some are not used for precious metals used in the jewellery industry, for example, and some may involve controlled atmospheres to prevent oxidation or to diffuse an element into the component surface or, conversely, out of the alloy. Carburizing of plain carbon steels to form a hard surface layer to give improved wear resistance is an example of diffusing carbon into the steel surface whilst Sage in 2010 gave us an example of diffusing oxygen out of the surface as a way of removing firestain from silver[2]. Diffusion bonding of different alloys together requires both temperature and pressure to achieve metallurgical bonding and is used to make materials for mokume gane[3,4]. This is an example of a diffusion heat treatment. Temperature and pressure are also used in Hot Isostatic Pressing to remove casting defects[24]. The point I make here is that the term 'Heat treatment' is a general term and is a process carried out for a variety of reasons.

Some of the types of heat treatment we use in our industry include:

1. **Softening treatments** (usually called 'annealing') to relieve internal stress and recover ductility. This includes full annealing, to recrystallize the microstructure, and stress-relief annealing to inhibit stress corrosion cracking in the carat golds. How we cool the alloy down after the heating cycle can be important too. Solution annealing and quenching in water is another that we use to get a softer condition that results from dissolving second phases back into the matrix phase or, simply, to obtain a higher temperature matrix phase. This is also the first stage of age-hardening treatments.

2. **Hardening treatments** to get additional strength by precipitation of finely-sized second phases within the microstructure. These second phases may be other solid solutions of the main alloying metal, but often these may be intermetallic phases, comprising two or metals in fixed proportions to produce a metal compound. In aluminum alloys, these may be aluminum-copper or -magnesium based compounds. We can take this approach to harden certain alloys of platinum, gold and even silver. In steels, we often precipitate carbides and nitrides in the microstructure to harden them. For silver-based electrical contact materials, we internally oxidize a silver-cadmium alloy by heating in an oxidizing atmosphere to form a dispersion of hard cadmium oxide particles within the structure. This hardens the alloy and improves erosion/wear during electrical switching operations.

3. **Diffusion treatments** are used for various reasons. Firstly, to homogenize alloy microstructures in terms of chemical composition, i.e. to remove segregation from casting. This involves heating to high temperatures, but below the solidus, for a long time. Another reason that we have already mentioned is to bond dissimilar alloys together. This also involves high temperatures for a period of time but additionally under pressure. The aim is to encourage atoms of each alloy to diffuse across the boundary into the other alloy, forming a strong metallurgical bond. Such techniques are also used for diffusion soldering[1]. We have also mentioned earlier the use of surface diffusion treatments to diffuse elements into the surface or to remove unwanted elements out of the surface.

4. **Decorative treatments**. I include here thermal treatments to oxidize the surface to produce decorative effects, as is used for some of the unusual colored golds[5] and to produce surface effects such as found with 'Spangold' alloys[6] which are based on a martensitic phase transformation. I do not intend to say more on these treatments in this presentation today.

ANNEALING

Annealing treatments are carried out to soften a cold-worked alloy, i.e. to restore some measure of ductility that has been lost due to the prior working. This may be to enable further working to be carried out without risk of cracking or fracture, or simply because a softer, stress-relieved condition is preferred. The term 'working' refers to mechanically deforming an alloy to change its shape. This may also result in the breakdown of a coarse microstructure. Working may be carried out hot or cold and I have discussed the difference between the two types of working recently[1].

To understand annealing treatments, we need to understand what happens to a metal or alloy when it is cold-worked and this, in turn, requires an understanding of the nature of metals and alloys. I will repeat here what I've said before, so some of you may find this section a little repetitive!

Nature of metals: Most metals and alloys (there are the odd exceptions) are crystalline, that is they are composed of many crystals bonded together to make the whole lump of alloy, Figure 1. Each crystal comprises atoms of the constituent metals arranged in some preferred crystal structure. For most precious metals, this is often the Face-Centered Cubic (FCC) structure, but other common metal crystal structures are Body-Centered Cubic (BCC) and Close-Packed Hexagonal (CPH). The importance of crystal structure with regard to working will be explained shortly. The relative size, shape and orientation of the crystals – or grains, as we metallurgists call them – are also important.
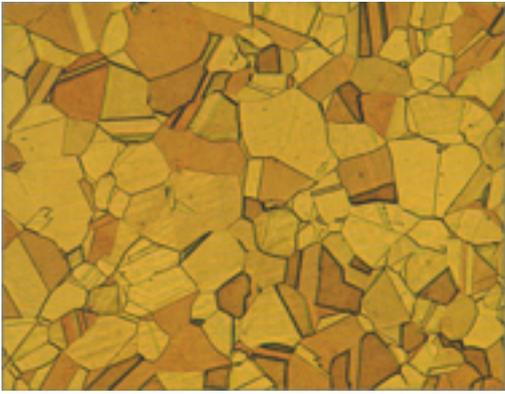
1.   Typical crystalline structure of metals & alloys of single phase (22 ct gold)

We also need to understand that pure metals and some alloys are single phase, i.e. they comprise crystals with all the same chemical composition and crystal structure. However, many alloys are more complex and contain two or more phases, i.e. crystals of different chemical composition and/or crystal structure, Figure 2. How such second phases are distributed, in terms of size and dispersion, within the microstructure has a big impact on the properties, too. It is the manipulation of such second phases within the microstructure that is at the heart of age-hardening treatments.


2.   Microstructure of a 2 phase cast silver-copper alloy

Deforming metals by cold working: By applying force, we can change the shape of a metal or alloy. We may do it simply by bending or hammering or by rolling, drawing, cupping, extrusion or forging in a machine. To accommodate the imposed shape change, the individual crystals must change shape too. In rolling, they become elongated and thinner. This is accomplished by preferred crystal planes within each crystal sliding over one another in more than one direction, i.e. in a complex way. The planes that slide are those that are closely packed with atoms and more widely spaced, because it is easier to break their interatomic bonds. In cubic crystals, there are clearly several equivalent planes which can slide over each other in several directions. We talk about 'slip systems' and their number (i.e. the number of equivalent planes X the number of slip directions). This is where the crystal structure plays a part: Face-centered cubic (FCC) crystal structures have more slip systems than body-centered cubic crystals (BCC) and, in turn, these have more than close-packed hexagonal (CPH) crystals. This is one reason why the precious metals tend to have good ductility – because they are FCC in structure!

When slip occurs, it does so by movement of planar crystal defects called dislocations, Figure 3, and as deformation proceeds, the number of dislocations multiplies and this hinders further slip, thus requiring a greater force to deform further. We call this work-hardening. It requires a lot less energy to slide crystal planes via dislocations as it only requires breaking of a single interatomic bond at a time, much like a zip moving along, undoing each interconnected 'tooth' one at a time.

Thus, a cold-worked metal is full of dislocations, i.e. there are a large number of crystal defects that make further sliding of planes more difficult and crack initiation more probable, leading to eventual fracture unless we take steps to reduce the number of dislocations. This is why we anneal!
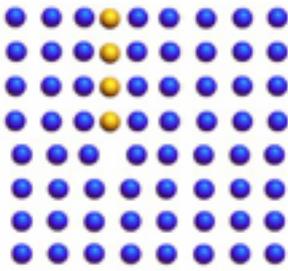
3.   Schematic: planar defects in the crystal lattice – dislocations

What happens when we anneal: Stage 1: As a cold-worked metal heats up to the annealing temperature, the dislocations start to become mobile and re-arrange themselves into a less energetic configuration. Where there is considerable cold work, they arrange themselves into a cellular structure with walls of dislocations around a core of material of low dislocation density, Figure 4. Each 'subgrain' is slightly mis-oriented compared to its neighbor within the deformed crystal. Typically, these cells are around a micron in size. This process of rearrangement helps to relieve internal stresses. This process is known as the recovery stage. As an example, we stress relieve anneal low carat gold alloys at a relatively low temperature of 250˚C for 30 mins to inhibit stress corrosion cracking. What we are doing is recovering the microstructure without fully annealing it. For nickel white golds, we prevent fire cracking during the heating stage of the annealing process by heating slowly up to about 300˚C to relieve residual stresses prior to heating up to the full annealing temperature of 750˚C.
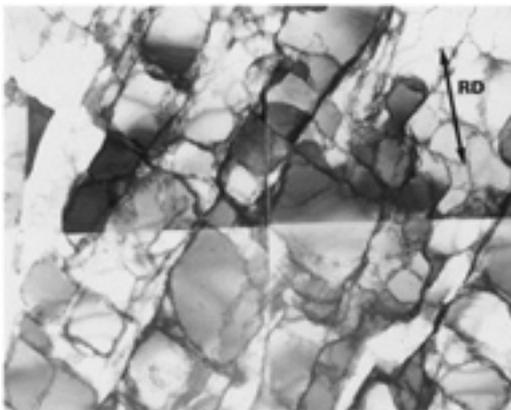
4.   Typical cell structure of deformed metals[23]

Stage 2: If we allow the temperature to increase to the full annealing temperature, then we see more rearrangement of dislocations and some of the cells begin to act as nuclei for new grain growth, particularly those at old grain boundaries and adjacent to hard particles or inclusions. These nuclei grow into the deformed regions of high dislocation density, eliminating them until all deformed material has been consumed and creating a new microstructure of soft, undeformed grains (crystals) with a low dislocation density. We call this process recrystallization. The new microstructure has restored the ductility, enabling it to be further cold-worked.

The number of nuclei formed will influence the final recrystallized grain size and depends on the amount of cold work and the annealing temperature. Lots of cold work and lower annealing temperatures favor a finer recrystallized grain size.

If we have second phases (or inclusions) present in the cold-worked alloy, these can affect the rate and temperature of recrystallization7. Coarse, widely spaced particles tend to accelerate the process whereas very fine, well-dispersed particles close together tend to inhibit the process due to their effect in pinning dislocations and stopping their movement. Thus, the process of recrystallization may take less time and/or occur at lower temperatures (acceleration) or take longer and/or occur at higher temperatures (inhibition), depending on the size and dispersion of the second phases in the cold-worked material.

Stage 3: If we continue to anneal at higher temperatures, the recrystallized grains will start to grow in size, with larger grains consuming smaller ones. We call this exaggerated grain growth and the well-known 'orange peel surface' effect we sometimes see in jewellery metals is a manifestation of this. This is a problem we often meet in torch annealing where we tend to overheat the metal as we cannot measure the annealing temperature easily or accurately.

Solution annealing: If we heat our metal to relatively high temperatures, but lower than the solidus temperature, we will tend to dissolve much of our second phases (in 2 phase alloys) back into solid solution, so the alloy tends to become single phase. I will illustrate this in terms of a simple phase diagram shortly. If we then cool rapidly, for example, by water quenching, there is insufficient time for the second phase to precipitate out again and we retain an essentially single phase microstructure that is metastable, i.e. it is a supersaturated solid solution. This condition is exactly what we need for age-hardening heat treatments.

Figure 5 is a simple phase diagram. It is the copper-silver phase diagram. We see that it is a simple eutectic system. The word 'eutectic' comes from the Greek and means 'easily melted'. What we see is a liquidus line in the shape of a valley that touches the solidus line at one point. This is the eutectic composition and at this point the liquid solidifies directly into a solid mixture of two phases. Note the eutectic temperature is lower than the melting point of the two pure metals.If we look at the Sterling silver composition of silver – 7.5% copper, we find that, at room temperature, it comprise two phases, a silver-rich solid solution as primary dendrites in the cast condition surrounded by a eutectic mixture of the silver-rich solid solution and a copper-rich solid solution. However, if we heat this alloy up to temperatures of about 800˚C, the second copper-rich phase re-dissolves back into the primary silver-rich phase (which can absorb more copper into its crystal structure at such high temperatures) and the alloy becomes single phase. Rapid cooling prevents the copper-rich phase from precipitating out again.

This process occurs whether the alloy is in an annealed or cold-worked condition. There is no growth of new grains involved.
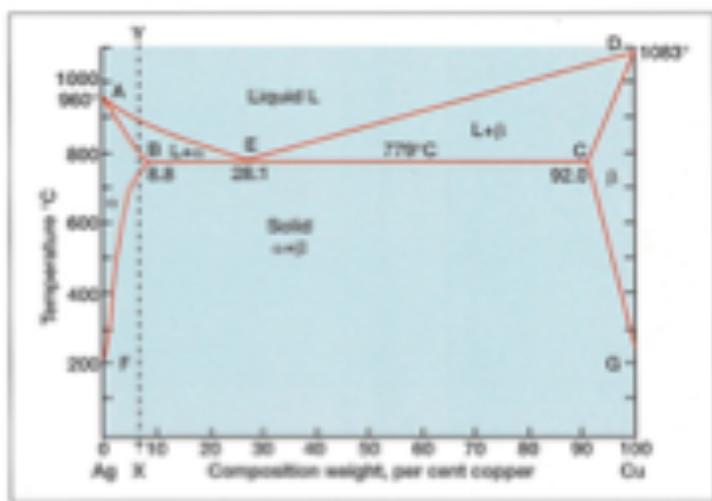

A simple phase diagram: the copper-silver system

AGE HARDENING

This heat treatment is also known as precipitation hardening or dispersion hardening since the aim is to precipitate out the second phase from the supersaturated solid solution in a controlled manner so that we obtain a fine dispersion of very small (submicroscopic) particles of the second phase within the crystals of the primary phase as well as on grain boundaries (which are preferred sites for precipitation), Figure 6. To achieve this, we need the alloy to be a supersaturated solid solution. If we anneal such an alloy structure at relatively low temperatures for a period of time, the second phase is nucleated and grows, i.e. it is precipitated out.
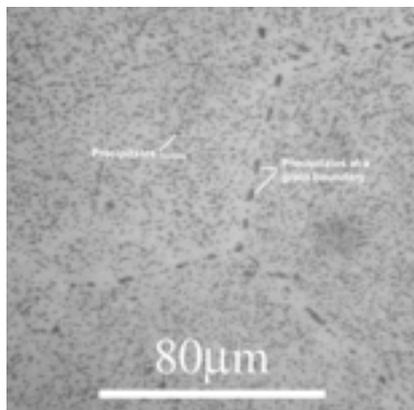
6.   Schematic: a typical age-hardening curve during the low temperature annealing stage (from Wright[11])

The lower the temperature, the more nuclei of second phase are formed that can grow but as diffusion rates are temperature dependant, the longer it will take to fully precipitate out. Thus, most age hardening treatments are a compromise of time and temperature. If we over-age, i.e. anneal for too long a time, the maximum hardness declines as the coarsening process of Ostwald ripening occurs, i.e. the precipitates grow in size at the expense of their number. A typical age hardening curve is shown in Figure 7.
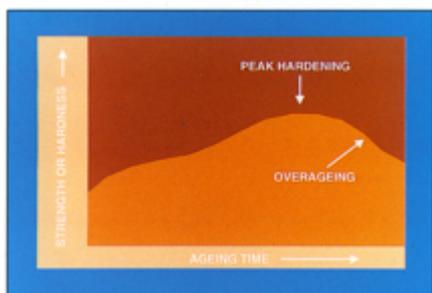
7.   Precipitates within grains after age hardening of microalloyed 24K gold, PureGold® (from Benadin[17])

Thus, the age-hardening process is a two-stage process: firstly, we need to solution anneal at high temperature for a short time to create the supersaturated solid solution and then cool rapidly to retain this condition and prevent the second phase from precipitating out in an uncontrolled manner. Then we perform the ageing heat treatment at low temperatures for a defined period of time to precipitate the second phase out as a fine dispersion of small particles, preferably within the grains, not just on grain boundaries, Figure 7.

Why do we want fine dispersions of small particles?: The answer is simply that many small particles of second phases (of different crystal structure and/or composition) dispersed within the primary crystals pin the dislocations and hinder their movement when stress is applied. The key is to create many small particles (at the micron or submicron size) that are close together, i.e. having a small interparticle spacing. Thus, it requires more force to be applied to move the dislocations past the particles to get slip of crystal planes and hence deformation. We have strengthened and hardened the crystal lattice!

Clearly, this hardening effect is greatest at ambient temperatures. If we stress or deform at higher temperatures, as in hot working, we coarsen the precipitates, increasing the interparticle spacing and so reducing their hardening effect, and eventually will dissolve them back if the temperature is sufficiently high, as in solution annealing. Simply put, such precipitates tend not to be stable at higher temperatures!

To digress a little: If we wish to have strengthening of an alloy operating at high temperatures (not important in jewellery applications, but very important in many engineering applications), then we need dispersions of particles stable at very high temperatures. These may be precipitates of second phases such as 'gamma prime' in nickel superalloys and carbides in alloy and stainless steels or, preferably, inert particles such as oxides. At high temperatures, we should note that there is more emphasis on stabilizing grain structure since grain boundary sliding is an important creep deformation mechanism at high temperatures. Hard particles also pin grain boundaries ('Zener' pinning). Hence, for nickel superalloy turbine blades, it is desirable to reduce grain boundaries and so directionally solidified or, better still, single crystal structures are preferred, as I have discussed previously[8].

**Examples of Age-hardening Heat Treatments:**

(1) Precious metals

A] Carat Gold
Most of you will be aware that for many copper-containing carat golds (up to 18ct), we can age harden them. There are 2 reasons for this: (i) the eutectic of the silver-copper system extends into the gold-silver-copper system to just beyond the 18ct level, giving regions of 2 phase alloys and (ii) we can take advantage of what we call an 'order/disorder' phase transformation that occurs in the gold-copper system at about 400˚C due to the formation of two intermetallic phases, AuCu and AuCu3. These ordered phases come about by the copper atoms taking up specific sites in the gold lattice which changes the crystal structure from face-centered cubic to face-centered tetragonal. These are hard and less ductile and it is more difficult for dislocations to move through the crystals. We should note that these phases can also dissolve small amounts of silver and so they extend into the gold-silver-copper system too.

Figure 8 shows an isothermal, horizontal section of the gold-silver-copper ternary phase diagram in which the 2 phase region deriving from the silver-copper eutectic system (see Figure 5) is shown at various temperatures between 700˚C and 350˚C. The main caratages are also marked as lines. In those areas outside of the contours, we have a single phase region.
Thus, for any caratage, the space on the lines between the 700˚ contour and the 350˚ contour represents alloys of that caratage where age hardening is possible. Actually, the range is considerably larger since we can solution anneal at higher temperatures, above the miscibility gap. McDonald and Sistare[9] produced a number of pseudo-binary phase diagrams, Figure 8, for this alloy system, showing clearly the regions in which age hardening is possible at each caratage. As Grimwade has pointed out[10], the situation is a little more complex because of the intrusion of the ordered phases, AuCu and AuCu3, into the ternary system.
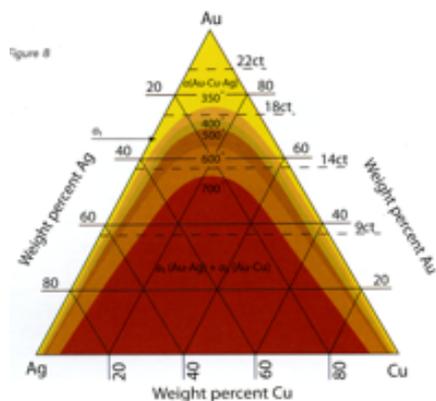
8.	Isothermal horizontal section of the ternary gold-silver-copper phase diagram showing the range of the 2 phase region at several of temperatures

We should note here that many commercial colored carat gold alloys contain other alloying metals such as zinc and these can impact the microstructure. Zinc tends to contract the 2 phase field9 and is used to improve the workability of carat golds, especially at 14ct. Thus, the region of composition in which age hardening is possible is reduced.

Typically, we solution anneal carat golds at temperatures above the immiscibility line (but below the solidus) and then age-harden at low temperatures in the range of 250˚C - 300˚C for a few hours. Table 1 shows the hardening effect of age hardening treatments on some carat golds, taken from Wright11. It is clear that we can get substantial hardening by ageing heat treatments, albeit at the expense of ductility. A red 18ct gold doubles it hardness and increases its tensile strength by 72%.

Table 1. Effect of age hardening on the mechanical properties of some 14ct and 18ct gold alloys (from Wright11)

Composition, % wt			Color	Condition	Hardness	Tensile Strength	Elongation
Oro	Ag	Rame		(Temp ˚C)	HV	N/mm2	%
58,5	20,5	21,0	Yellow	Annealed 650,WQ	190	580	25
				Aged 360, 1h	270	800	3
58,5	10,0	31.5 (Cu/Zn)	Pink	Annealed 650,WQ	148	440	35
				Aged 300, 1h	242	593	3
58,5	9,0	32,5	Red	Annealed 650,WQ	160	550	45
				Aged 260, 1h	260	700	12
75,0	12,5	12,5	Yellow	Annealed 550,WQ	150	520	40
				Aged 280, 1h	230	750	15
75,0	9,0	16,0	Pink	Annealed 550, WQ	160	550	40
				Aged 280, 1h	285	850	7
75,0	4,5	20,5	Red	Annealed 550, WQ	165	550	40
				Aged 280, 1h	325	950	4

WQ – water quenched.

The amount of age hardening we can obtain will depend on the copper content, as shown in Figure 9 for 14ct gold alloys.
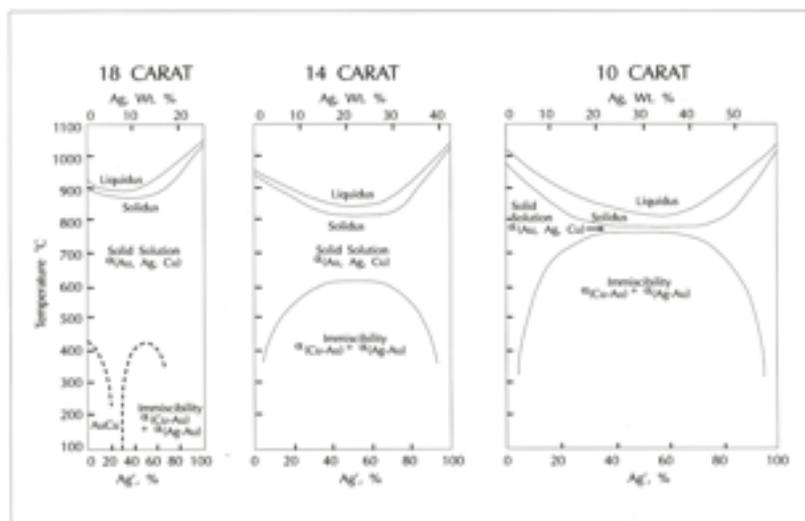
9.   Age hardening of 14ct golds (from Wright[11])

Other carat gold alloys can also be age hardened. For example, the '990' gold alloy, containing 1% titanium, can be hardened to HV170 after annealing for 1 h at 500˚C, compared to only HV70 in the annealed condition12. Solution treatment is carried out at 800˚C for 1 h and water quenching, prior to ageing. The precipitate is the intermetallic AuTi4. Some of the micro-alloyed 24ct golds can also be age-hardened13. Nickel white golds have a miscibility gap, i.e a 2 phase region, in the gold-nickel-copper phase diagram and so many nickel white alloys are capable of age-hardening. However, one phase is a yellow gold-copper phase and leads to a loss in whiteness.

B] Silver

As mentioned earlier, sterling silver (silver- 7.5% copper) is capable of being age-hardened, as discussed by Grimwade10 and Reti14. Solution annealing is carried out at about 730˚C followed by quenching in water. Ageing is then carried out at 300˚C for 1h. This raises the hardness to HV140 from an annealed hardness of about HV70. However, such treatment cannot be applied to silver items that have been soldered, since soldering temperatures are normally below the solution treatment temperature. Thus, solder joints would melt on solution annealing. The higher silver content alloys such as Britannia silver (95.8% silver- copper) should also be capable of some age hardening.

Some of the new firestain resistant alloys such as Argentium® can be age hardened, forming precipitates of a copper-germanium compound, Cu5Ge15. Aged at 300˚C, a hardness of HV120 can be achieved. Likewise, microalloyed PureSilver16,17 can be age hardened.

C] Platinum

Most standard 950 or 900 platinum alloys are single phase alloys and so are not age hardenable18. However, the platinum- 5% gold alloy should be capable of some age hardening as there is a large miscibility gap in the phase diagram that extends at room temperature almost to pure platinum. An aged hardness of HV300 versus HV90 in the annealed condition is reported in reference 18.

There are several commercial platinum alloys that contain gallium as an alloying metal (e.g. see Table 9 in reference 18) and these are all capable of being age-hardened. For example, the 'HTA' alloy containing 4.8% (gallium + indium + copper) attains a hardness of HV340 – 360 when aged at 700˚C compared to HV180 in the annealed condition18, 19.

D] Palladium

The nature of the commercial alloys is not clear as yet18. Some contain rhodium and/or gallium which have limited solid solubility and may just be in a 2 phase region, but it is unlikely that there will be much response to an age-hardening heat treatment. But improved alloys that are age hardenable may yet be developed.

(2) Base metal alloys

I am going to take some examples of typical base metal alloys used in the engineering industries, an aluminum alloy, a copper alloy and a titanium alloy to demonstrate that age hardening treatments are pretty universal.

E] Aluminum alloys

There are several basic ranges of aluminum alloys used in the engineering industries based on their main alloying metals. Two of these are heat treatable (i.e. age hardenable) series of alloys, the 2XXX series which are aluminum-copper alloys and the 7XXX series which are aluminum-zinc-magnesium alloys. I will give one such example here of a 2XXX Al-Cu based Alloy.

Firstly, the basics: Figure 10 is a section of the aluminum – copper phase diagram and shows a typical sequence of microstructure development during a hardening heat treatment of a 4% copper alloy, which is 2 phase at ambient temperatures, comprising primary aluminum solid solution of kappa phase and theta phase which is CuAl2. Solution treatment at about 550˚C gives rise to a single phase alloy, κ (kappa) phase solid solution. This is retained as a supersaturated solid solution on water quenching. Ageing at low temperatures, say 200˚C, results in the precipitation of sub-microscopic particles of θ (theta) phase, which cannot be seen in the optical microscope. However, overaging for long times causes particle coarsening and these then become visible with a consequent loss of hardening.
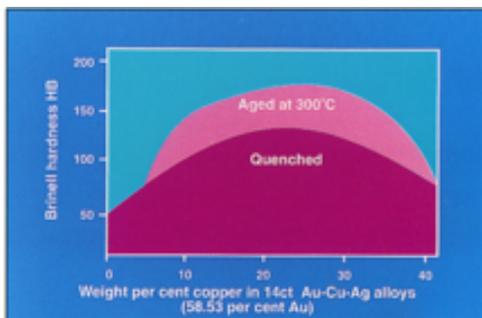
10.   The aluminum corner of the aluminum-copper phase diagram and the effect
of heat treatment on the microstructure (taken from reference 21)

The AA2618 wrought aluminum alloy contains 2.5% copper-1.5% magnesium-1.0% nickel-1.0% iron – 0.1% titanium and is strengthened by an age hardening heat treatment; it has good high temperature properties. It is used in many aeronautical applications including forgings and was developed for application in the supersonic Concorde aircraft.

Age hardening to the T61 condition (ASTM specification) is typically carried out by solution annealing at about 530˚C for 30 mins, water quenching and then ageing at about 200˚C for 20 hours. Table 2 shows the hardening effect. The hardening precipitates are Al9FeNi. Figure 11 shows a typical age hardening curve, with ageing carried out at 200˚C on forged compressor wheels for diesel turbochargers20. A peak hardness of HV150 is attained at about 17 hours, with a clear drop in hardness seen at longer ageing times, illustrating the over-ageing due to particle coarsening.

Table 2. Effect of Age Hardening on the yield stress and hardness of Aluminum alloy AA2618

Condition	Yield Stress, MPa	Hardness, HV
Solution treated	120	75
Age hardened	370	140

Solution treated at 530˚C for 30mins, WQ and aged at 200˚C for 20h
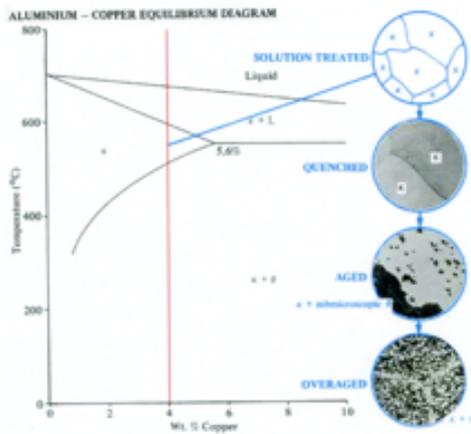
11.   Age hardening curve for AA2618 aluminum alloy, aged at 200˚C (after solution annealing at 530˚C) (from reference 20)

F] Copper Alloys

Age hardening plays an important role for hardening several copper alloys, including those for electrical contact and thermal conductivity applications. Precipitation of second phases helps to maximize electrical and thermal conductivity of the copper matrix phase. Amongst such alloys are copper-beryllium, copper-chromium, copper-zirconium and copper-chromium-zirconium alloys. I will take a copper-chromium alloy as an example.

The copper corner of the Cu-Cr phase diagram, Figure 12, shows the limit of solid solubility of chromium in copper is very low but rises to about 0.5% at the liquidus temperature, circa 1200˚C (2190˚F). A typical commercial alloy used for spot welding electrodes, for example, is alloy C18200, which contains 0.6 – 1.2% chromium. It is a 2 phase alloy, comprising primary copper-rich alpha phase and a chromium-rich beta phase. It is normally used in the age hardened and worked condition. Typical properties, Table 3, show an approximate doubling of hardness and strength after age hardening. This can be further increased by subsequent cold working.
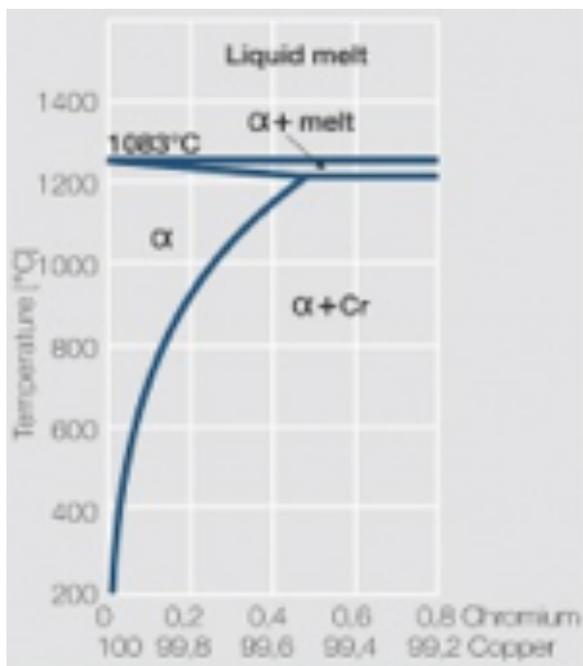
12.   Copper-chromium phase diagram (from reference 22)

Table 3. Effect of heat treatment on the mechanical properties of a copper-chromium alloy C18200

Condition	Hardness, HV	Yield Strength, (0.2% proof), kg/mm^2	Tensile Strength, kg/mm^2	Elongation, %
Solution treated	68	10	24	30
Solution treated & cold worked	115-130	18 -30	30 -41	4 -7
Solution treated and aged	115	30	42	15
Solution treated, aged & cold worked	135-170	37-51	42-55	2-12

Typical solution treatment temperature is 980˚C (1796˚F), water quenched. Typical age hardening temperature is 425 - 500˚C (797- 932˚F) for 2-4 h

G] Titanium Alloys

The most common commercial aircraft alloy is probably the alloy Ti-6Al-4V, i.e. a titanium alloy containing 6% aluminum and 4% vanadium. It is a 2 phase alloy comprising alpha solid solution which has a close packed hexagonal (CPH) crystal structure and beta solid solution which is a body-centered cubic (BCC) higher temperature phase. Aluminum stabilizes the alpha phase whilst vanadium stabilizes the beta phase. The alloy transforms entirely to beta phase at about 980˚C, as shown in the pseudo binary phase diagram (Ti-6% Al) - V, Figure 13. The microstructure is capable of considerable manipulation by varying heat treatments. Typically, the alpha phase precipitates out in a lamellar mode when cooled from the beta phase region, but this can be coarse or fine and can also be transformed in a martensitic structure.
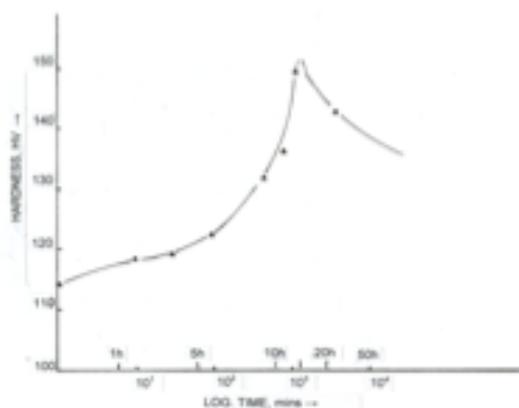

13.   Pseudo binary phase diagram for Ti-6Al-4V alloy as a function of V content

This alloy is typically used in one of 4 metallurgical conditions:
•   Mill annealed - typically 1-4h at 705-790˚C, air cooled)
•   Duplex annealed - e.g. 10min at 940˚C, water quenched + 4h at 675˚C, air cooled
•   Solution treated and aged, 'STA' - typically 10min at 940-970˚C, water quenched + 2-8h at 480-595˚C, air cooled
•   Solution treated and overaged, 'STOA' - typically the same as STA but aged for longer times to coarsen the precipitates

Which condition is used depends on what balance of mechanical properties are required at the operating temperature. Table 3 shows the effect of such heat treatments on the room temperature tensile properties of isothermally forged material, deformed in the superplastic regime at about 950˚C20. As might be expected, isothermally forged alloy is essentially in the fully annealed condition, so mill annealing (recrystallization annealing) has little effect, but solution treatment and aging ('STA' condition) improves strength at the expense of ductility, but the effect is not so large as we have seen for other metals. The duplex annealed condition is an age hardening process but the ageing is done at higher temperatures, giving a coarser dispersion of lamellar alpha phase.
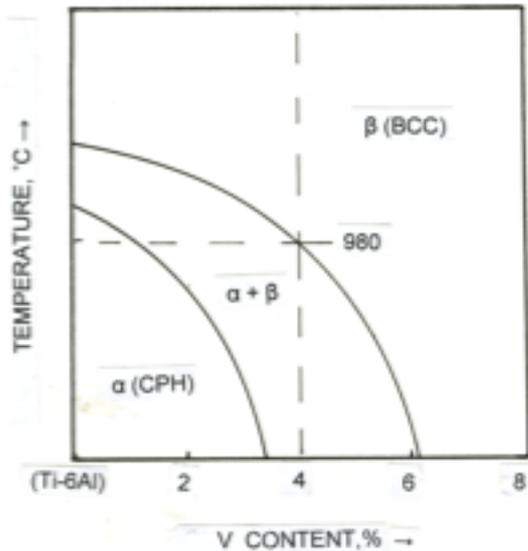
14.

Table 4. Effect of various heat treatments on tensile properties of isothermally forged Ti-6Al-4V alloy at 20˚C

Condition	Yield stress (0.2% proof), MPa	Tensile strength, MPa	Elongation, %
As isoth. forged	955- 968	1018-1037	15.1-17.7
Mill annealed	975	1028	15,7
Duplex annealed	1033	1084	13,5
STA	1118	1195	10,6

Mill annealed: 2h at 725˚C (1337˚F), air cooled

Duplex annealed: 10min at 940˚C (1724˚F), water quenched + 4h at 675˚C (1247˚F), air cooled

STA (solution treated & aged): 10min at 940˚C, water quenched + 4 h at 540˚C (1004˚F), air cooled

CONCLUDING COMMENTS

This presentation has focused on heat treatment of the jewellery precious metal alloys and attempts to show that the term is a general one covering a broad range of thermal treatments. In particular, it has focused on annealing and age hardening treatments and what they entail, with emphasis on the scientific principles that underpin them. The focus has been the changes in mechanical properties that result.

These treatments are also widely used in other base metal alloys for engineering applications and typical examples of age hardening treatments of commercial alloys have also been shown.

ACKNOWLEDGEMENTS

REFERENCES

Note: Papers presented at the Santa Fe Symposium can be downloaded free from the website: www.santafesymposium.org

1.Christopher W Corti, "Basic metallurgy of the precious metals – Part IV: Deformation processing, joining and corrosion", The Santa Fe Symposium on Jewelry Manufacturing Technology 2014, ed. Eddie Bell (Albuquerque: Met-Chem Research, 2014), 111-137.

2.Patrick Sage, "Firescale prevention and removal", The Santa Fe Symposium on Jewelry Manufacturing Technology 2010, ed. Eddie Bell (Albuquerque: Met-Chem Research, 2010), 423-437

3. For example, James Binnion, "Non-traditional Mokume Gane materials: diffusion bonding of iron to precious metals", The Santa Fe Symposium on Jewelry Manufacturing Technology 2004, ed. Eddie Bell (Albuquerque: Met-Chem Research, 2004),87-104.

4.For example, Chris Ploof, "Mokume Gane bonds: The effect of quenching on bond strengths", The Santa Fe Symposium on Jewelry Manufacturing Technology 2014, ed. Eddie Bell (Albuquerque: Met-Chem Research, 2014), 389- 401

5.Christopher W Corti, "Blue, Black and Purple! The Special Colours of Gold", The Santa Fe Symposium on Jewelry Manufacturing Technology 2004, ed. Eddie Bell (Albuquerque: Met-Chem Research, 2004), 121-133. Also, "Blue, Black and Purple! The special colours of gold & other Precious Metals", Presented at the Jewellery Technology Forum, Vicenza, Italy, 15th January 2012. See also: C W Corti & E Van de Lingen, "Special colors of precious metal jewellery", The Santa Fe Symposium on Jewelry Manufacturing Technology 2016, ed. Eddie Bell (Albuquerque: Met-Chem Research, 2016),165-197

6.Mike Cortie et al, "Spangold – a jewellery alloy with an innovative surface finish", Gold Technology, No. 14, November 1994, 30-36

7.Christopher W Corti, PhD thesis, "Some aspects of the recrystallisation of dispersion-strengthened iron-alumina alloys", University of Surrey, U.K., May 1973; C W Corti & P Cotterill, "A re-examination of the data for the recrystallisation of copper crystals dispersed with silica", Scripta Met.,1972, 6, 1047-1050

8. Christopher W Corti, "Basic metallurgy of the precious metals, Part II – Development of Alloy Microstructure through Solidification and Working", The Santa Fe Symposium on Jewelry Manufacturing Technology 2012, ed. Eddie Bell (Albuquerque: Met-Chem Research, 2012), 123-144

9. A S McDonald and G H Sistare, ""The Metallurgy of some Carat Gold Alloys", Gold Bulletin, 11 (3), 1978, p66 [This can be downloaded free from archive in http://link.springer.com/journal/13404/11/3]

10. Mark Grimwade, Introduction to Precious Metals, Brymorgen Press, Maine, USA, 2009. ISBN978-1-929565-30-6

11. John C Wright, Technical Manual for gold jewellery, World Gold Council, London, 1997, reprinted 2001 [pdf files available from World Gold Council & myself]

12. See issue on '990 Gold', Gold Technology, No 6, May 1992. [pdf files of this issue can be obtained from World Gold Council, London, e-mail: industry@gold.org]

13. Christopher W Corti, "Metallurgy of Microalloyed 24 carat Golds", The Santa Fe Symposium on Jewelry Manufacturing Technology

1999, ed. Eddie Bell (Albuquerque: Met-Chem Research, 1999), 379 - 402. Also: Gold Bulletin, 32 (2), 1999, 39-47. [This can be downloaded free from archive in http://link.springer.com/journal/13404/11/3]

14. Aldo Reti, "Understanding sterling silver", The Santa Fe Symposium on Jewelry Manufacturing Technology 1997, ed. Dave Schneller (Albuquerque: Met-Chem Research, 1997), 339-356

15. Peter Johns, "Firestain resistant silver alloys", The Santa Fe Symposium on Jewelry Manufacturing Technology 1997, ed. Dave Schneller (Albuquerque: Met-Chem Research, 1997), 33-67

16. Christopher W Corti, "Microalloying of High Carat Gold, Platinum and Silver", presented at the Jewellery Technology Forum, Vicenza, Italy, 17-18th June 2005. Publ. in conference proceedings.

17. John Bernadin, "Understanding Microalloys", The Santa Fe Symposium on Jewelry Manufacturing Technology 2005, ed. Eddie Bell (Albuquerque: Met-Chem Research, 2005) , 53-64.

18. Christopher W Corti, "Basic Metallurgy of the precious metals-Part I", The Santa Fe Symposium on Jewelry Manufacturing Technology 2011, ed. Eddie Bell (Albuquerque: Met-Chem Research, 2011), 145-181

19. Greg Normandeau & David Ueno, "Understanding Heat Treatable Platinum Alloys" in The Santa Fe Symposium on Jewelry Manufacturing Technology 1999, ed Dave Schneller (Albuquerque: Met-Chem Research, 1999), 73-103

20. Christopher W Corti, Internal reports, Brown Boveri Research Centre, Switzerland, 1977

21. Sourced from http://hsc.csu.edu.au/engineering_studies/focus/aero/2580/aluminium_alloys.html

22. Sourced from http://www.electrical-contacts-wiki.com/index.php/Precipitation_Hardening_Copper_Alloys

23. Sourced from N Hansen & D Juul Jenson, Materials Science & Technology, 2011, 27 (8), 1229-1240, publ. by Maney Ltd

24. Teresa Fryé, The effects of hot isostatic pressing of platinum alloy castings on mechanical properties and microstructures",
The Santa Fe Symposium on Jewelry Manufacturing Technology 2014, ed. Eddie Bell (Albuquerque: Met-Chem Research, 2014), 189-209