BASIC METALLURGY OF THE PRECIOUS METALS: PART II - DEVELOPMENT OF MICROSTRUCTURE THROUGH SOLIDIFICATION, WORKING AND ANNEALING

Dr. Christopher W. Corti
COReGOLD Technology Consultancy
Reading, UK

CORTI

PREFACE

In Part I last year, the effect of alloying on the various properties of the jewelry precious metals and their alloys was examined and related to microstructure through an understanding of phase diagrams – the Metallurgist's 'road maps' of alloying behavior. The influence of working and annealing on properties was mentioned but not discussed. We noted that properties, alloy composition and microstructure are all interrelated.

In this second part, we focus more on the alloy macro- and micro-structures and how they are affected by its processing history – solidification conditions, working and thermal treatments – which, in turn, influences the final properties. We look at metal integrity, microstructure development and defect formation during casting and working and how microstructure is important to both manufacturing and service performance.

INTRODUCTION

In Part 1 of this series of presentations last year, we looked at the nature of metals and the effect of alloying on properties. This year, I want to focus more on alloy macro- and micro-structures. How we can influence them by casting, by mechanical working and thermal treatments (aka annealing)? Why are they important?
As always, I must acknowledge the contribution of Mark Grimwade to our industry in teaching us about basic metallurgy over the years. His approach to the topic has influenced my own.

Let me start by asking you a question or two:
Question: Do we prefer to have an as-cast piece or a wrought piece

of jewelry in a particular alloy. Which is stronger or more ductile? Is there a difference? Another question: Can we change the strength and ductility of an 18K red gold through the way we process it? My presentation today hopefully will try and answer these and other questions.

As I noted in my Basic Metallurgy – Part I presentation last year[1], anyone involved in the making of jewelry should have an appreciation of the nature of the metals and alloys with which they work and understand how alloying and processing of the metals influences the microstructure and consequently their properties. For jewelry, we focus on the alloys of the precious metals – gold, silver, platinum and palladium, all four of which are inherently ductile metals - but what I say is of general validity and applies to most metals.

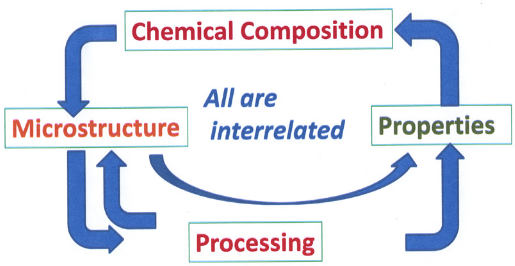


Figure 1: Interrelationship of alloy composition, microstructure and processing history on properties (schematic)

Two fundamental points to understand are that:

- Alloy composition, microstructure and processing history are interrelated, Figure 1, and jointly influence an alloy's properties, be they chemical (e.g. corrosion and tarnish resistance), physical (e.g. density, color) or mechanical (e.g. strength, malleability, hardness). These, in turn, influence manufacturability and service performance.
- Most metals and alloys are composed of many crystals, or grains as we metallurgists call them; thus, most alloys are polycrystalline. There are some rare exceptions such as single crystal aero turbine blades and amorphous or glassy metals such as were described here last year by Houghton[2] and earlier in 2007 by Lohwongwatana[3].

IMPORTANCE OF GRAIN SIZE TO JEWELRY

As jewelers attending The Jewelry Symposium and earlier Santa Fe Symposia will know, metallurgists pay some attention to the crystal, or grain, size in their alloys. We talk about 'large (or coarse) grains' or small (or fine) grain sizes and generally state the desirability of the latter in terms of jewelry production. The terms 'large' and 'small' are, of course, relative. But for practical purposes, 'Large' will usually mean grains of the order of millimetres or larger and 'small' will refer to grain sizes of the order of tenths or hundredths of a millimetre (10 – 100 microns). You may also hear of grain sizes referred to in terms of an ASTM numerical value. This is a comparative method of measuring grain size. The higher the number, the smaller is the grain size.

Why is control of grain size (and their shape) important? Well, it is down to the relation between the grains (crystals) and the grain boundaries – the region at the junction of adjacent grains - and their relative influence on mechanical deformation processes. Grain boundaries are where the atoms sitting on the crystal lattices of adjacent grains do not match across together, creating a narrow region of imperfect crystal, Figure 2. Often, these can be a preferred site for deleterious impurities and second phases, leading to embrittlement. At low or ambient temperatures, the deformation process under an imposed load is governed mainly by the dislocation slip mechanism within each grain (dislocations are linear crystal defects responsible for deformation on crystal slip planes). Without going into deep explanations, the outcome is that alloys with finer grains are stronger than those with large grains, and this effect is expressed by the Hall-Petch relationship in which yield strength, $\sigma_{y.s.}$, is inversely related to the grain size squared:

$$\sigma_{y.s.} = m/d2$$

where d is the average grain diameter and m is a constant. The yield strength of a material (known also as the Elastic limit) is the stress required to start plastic deformation and is smaller than the ultimate tensile strength ('UTS').

Figure 2: Schematic: Atomic structure at a grain boundary

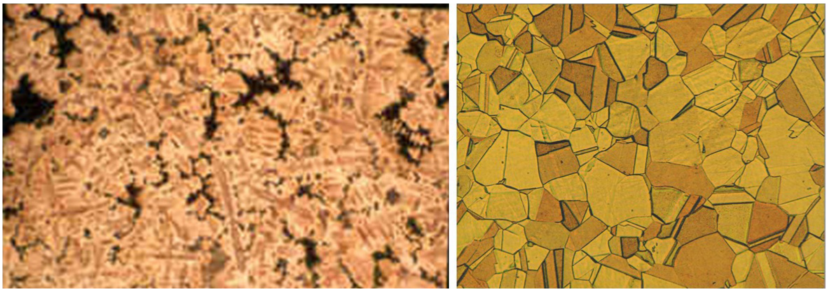
CORTI

Thus, the jewelry is stronger and harder if it is fine-grained and, beneficially, it is also more ductile and less prone to cracking, impurity embrittlement and the 'orange peel' surface after deformation. As jewelry is generally only subject to relatively simple stresses (loads) at ambient temperatures, whether in a production environment or in service, a fine grain size is therefore desirable. It is why grain refiners are used in jewelry alloys. This is generally true for other non-precious engineering components such as sheet steel for car bodies and white goods.

On the other hand, engineering components can be subjected to often-complex stresses over long periods at high temperatures. For example, turbine blades and disks in jet engines and boiler tubes in utility power stations. At these high temperatures, the main deformation mechanisms are phenomena such as creep and fatigue. Creep is the slow deformation under a steady low stress or load and fatigue is the mechanical failure under an alternating load. The lead on a Church roof, sealing the edges of its tiled roof, is actually at a hot working temperature and so slowly creeps under its own weight. Under such conditions, the grain boundaries are weaker and grains can slide over each other; hence, a large grain size is preferred as there is relatively less grain boundary area. In the ultimate, such as gas turbine blades, we prefer to eliminate grain boundaries, so we find use of directionally solidified alloys with elongated grains and even single crystal alloys for optimum creep and fatigue strength. An extreme of fine grain sizes is a phenomenon known as superplastic deformation, whereby alloys with stable, fine grain sizes can be gently deformed at temperature under low stresses to very large deformations, just like Swiss cheese fondue. Several titanium aircraft components of complex shape are manufactured by this technique including the very large fan blades on Rolls Royce jet engines. Interestingly, fine-grained sterling silver can be superplastically deformed under the right conditions[4] and I would expect some other precious metal alloys also to do likewise. But to date, that ability has not been developed or commercially exploited in our industry.

EXAMINATION OF MICROSTRUCTURE: METALLOGRAPHY

As many of you will also know, we can examine the microstructure and measure the grain size of a piece of jewelry metal. Due to the scale of this, it is often performed under an optical microscope. The process of examining grain size and general microstructure is called 'metallography'. Figure 3 shows the microstructure of both as cast and cold worked and recrystallized gold alloys. There are obvious differences in appearance and these will be explained later.



(a) (b)

Figure 3: Microstructure of typical karat gold alloys (a) as cast, (b) worked and annealed

Normally, if we wish to examine the macrostructure or microstructures of an alloy, we need a flat polished surface as optical microscopes have a limited depth of focus. In order to expose the features such as grain boundaries and second phases, we often need to etch the surface with a corrosive liquid such as acid. As grain boundaries are less perfect than the crystals, they etch preferentially to reveal themselves. As different crystals are oriented in different directions relative to the plane of the surface, they also etch at different rates and so appear of different contrast or color to the eye. Where more than one phase is present, these also etch differently and usually show themselves as different colors or shades of darkness.

If we need greater magnification than we can get in an optical microscope to see the features of interest or have an uneven surface such as a fracture, then we use a scanning electron microscope (SEM) which has a larger depth of focus and can magnify to a much greater extent. Here, flatness of the surface is not such an issue as in optical light microscopy and we can often see different phases by atomic number contrast, without the need for etching (see figure 22 in reference 5, for example)[5,6]. The heavier elements appear whiter under the SEM and the lighter ones darker, so giving rise to differences in contrast with varying alloy phase composition.

CASTING

Casting is a process for producing alloys of the desired composition and also for specific shapes. These can be either net shapes, as in investment (lost wax) casting, or stock materials, i.e. ingots or continuously cast rods, that can be further processed to modify the shape, structure and properties. Casting involves melting and the solidification of molten metal. Subsequent mechanical processing of ingot materials enables us to break down coarse, non-uniform structures to more desirable refined structures, better suited to the purposes that we require in manufacture and in subsequent service and, generally, with improved, more consistent properties.

The structure of cast alloys depends on the rate at which we cool and solidify the metal which, in turn, depends on the size of the casting and the thermal conductivity of the mold material. Thus, the structure of large ingots will differ from that of small investment castings. We will explore the influence of casting conditions shortly.

Solidification

As has been mentioned before[7,8], pure metals solidify at a fixed temperature; for example, gold solidifies at 1064°C/ 1947°F and silver at 962°C/1763°F. Most alloys*, on the other hand, solidify over a temperature range: the liquidus temperature is the temperature above which the alloy is completely molten and is the temperature at which solidification starts on cooling; the solidus is the temperature at which solidification is completed and thus below this temperature the alloy is completely solid. Between the liquidus and solidus, alloys comprise some liquid and some solid, often known as the 'mushy' or pasty state. The characteristics of solidification and the resulting structure are influenced by the temperature gap between the liquidus and solidus and the overall phase diagram for the alloy system.
[*There are a few exceptions, such as eutectic alloys which also solidify at a fixed temperature like the pure metals]

To understand the process of solidification, it helps to understand the atomic structure of liquids and how atoms coalesce to form solid material. The liquid state comprises mobile atoms in a dynamic, unstructured state. Some atoms will come together briefly to form a small cluster but these quickly break up.

As we cool a liquid (molten metal in our case), small clusters of atoms come together and stay together to form a nucleus. The formation of nuclei tends to occur at preferred sites such as a mold wall or at impurity particles/inclusions but can occur randomly in the melt. As the temperature falls, more atoms join the small stable clusters of atoms that comprise the nuclei in a structured way that is the crystal lattice of that metal or alloy. For our precious metals, that will be in the face-centred cubic arrangement, discussed in Part I[1]. These are the embryonic crystals that will make up our alloy. A fast cooling rate during solidification will lead to more nuclei forming and consequently, because each nucleus develops into a crystal or grain, a fine grain size results. A slow cooling rate leads to less nuclei forming and a resultant larger grain size. We should note that nucleation at inclusion particles is how insoluble grain refiners like iridium and ruthenium work in gold alloys, for example, by promoting nucleation.

These nuclei grow by adding more atoms from the liquid. They do so in preferred crystal directions, extending from the cube faces and branching out as the crystal grows. This results in a tree-like structure that we call a dendrite. All the nuclei grow into dendrites, each of which will have an orientation dependent on the orientation of the original nucleus. Each dendrite continues to grow until it collides with an adjacent dendrite. The interface between them forms a boundary. This we call the crystal boundary or, more usually, a grain boundary. Here, the atoms on each lattice do not fit together cleanly, so creating a thin region of imperfect crystal, as we have discussed earlier. Figure 4 shows some dendrites in a platinum alloy[9]. We can clearly see several dendrites, each pointing in different directions. We often see such dendrites in shrinkage cavities in investment casting. Provided there is feeding of more liquid metal, the spaces between dendrites eventually fill up to give solid metal. If there is restricted feed, then shrinkage cavities (porosity) will result.

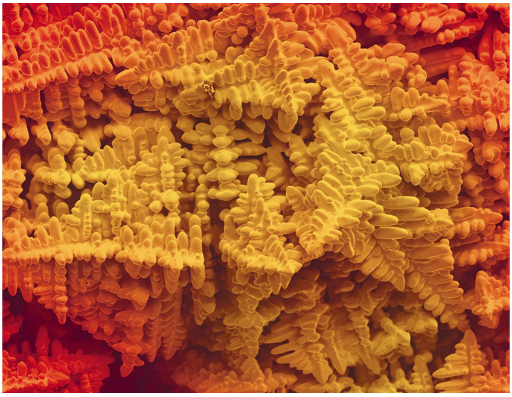


Figure 4: SEM image of dendrites in Pt-Ru alloy, seen in a shrinkage cavity (from reference 9)

If we examine an etched metallographic section of a cast metal under the microscope, such as that shown in Figure 3(a), we can clearly see the dendritic structure. We also note that the dendrite center etches up differently to the outer zone; this is due to chemical segregation, whereby the metal that solidifies first has a different chemical composition from that which solidifies last. This is known as 'coring'. Why that is so, we can readily explain from the phase diagram[8].

In Figure 5, we examine a binary phase diagram such as the gold-silver system for simplicity. If we take alloy X indicated by the vertical line and follow it down as the temperature decreases, when it hits the liquidus at 'M', solid alloy of the composition indicated where a horizontal line from this point intersects with the solidus line at 'N' is formed. As the temperature is lowered, the composition of solidifying metal moves down the solidus line towards the vertical line, where it meets the solidus at 'P' (with some undercooling, this occurs at a lower temperature, indicated at 'R'). Thus, the larger the gap between the liquidus and solidus, the larger is the composition difference between the center and outside of the dendrite. We can remove this composition difference by a high temperature homogenising annealing treatment which allows for interdiffusion of atoms to occur.

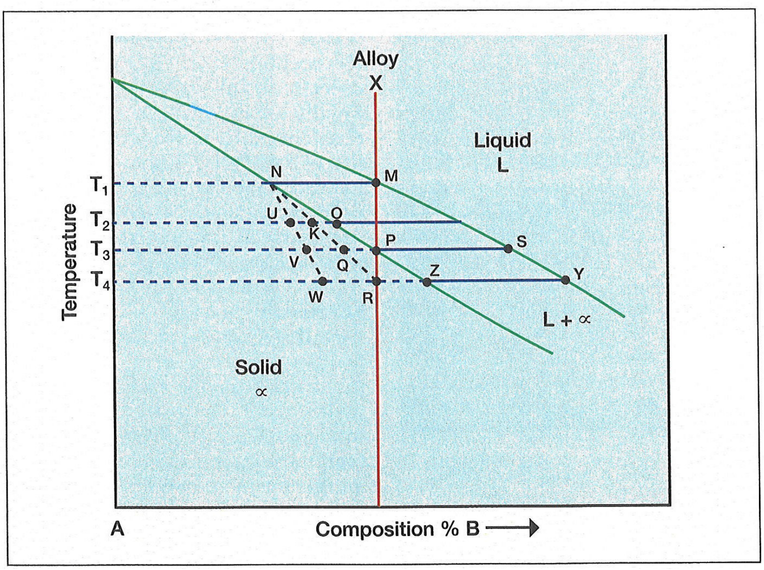


Figure 5: Non-equilibrium cooling, leading to coring in solid solutions (schematic), from reference 8

When we pour molten metal into a mold, it begins to solidify inwards from the mold walls as this is the coldest temperature. If a cold metal (e.g. iron) mold is used, as is usual for ingot casting, the rate of heat removal is rapid. Initially, a thin layer of fine grains is formed – the chill layer - because of the high rate of nucleation.

Then long finger-like grains – called columnar grains – begin to grow inwards from the chill layer towards the center of the ingot, Figure 6.

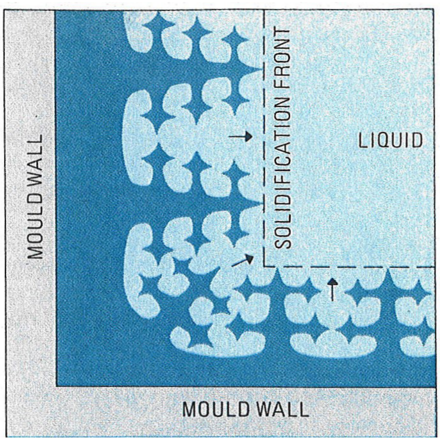


Figure 6: Solidification proceeds inwards from the colder mold walls

If the metal casting temperature is relatively high, this columnar growth will extend into the center of the ingot, Figure 7. This is not a good structure if you are going to roll the ingot to plate or sheet, as it may split down the middle (known as alligatoring, Figure 8), as this is also where impurities will tend to concentrate as it is the last metal to solidify.

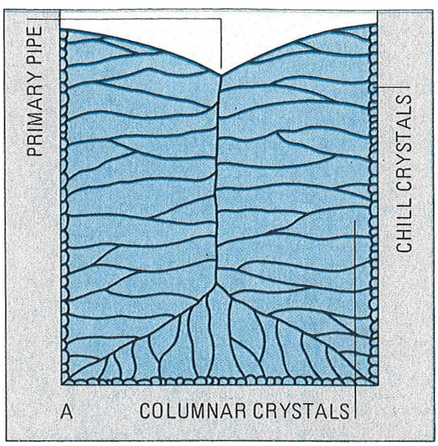


Figure 7: Grain structure of ingots cast into metal molds at a relatively high pouring temperature. Columnar grains grow into the center of the ingot.

On the other hand, if the metal casting temperature is low, nucleation will eventually take place generally throughout the remaining liquid metal before the columnar grains can reach the center and we find a more equiaxed grained zone in the central region, Figure 9, which is a better structure.

When a ceramic (plaster) mold is used, as in investment (lost wax) casting, the cooling rate is markedly slower (due to the lower thermal conductivity of the ceramic) and equiaxed grains are formed throughout the casting. This is a preferred microstructure.

Figure 8: Splitting of gold alloy ingot down the center during rolling ('alligatoring')

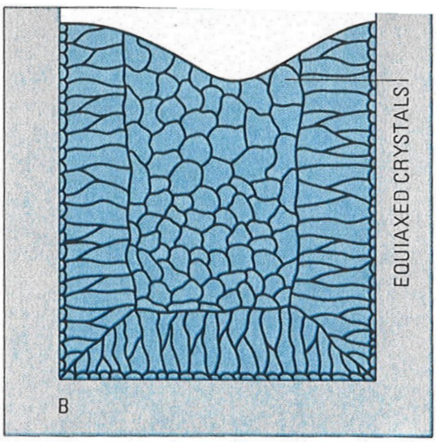


Figure 9: Grain structure of ingots cast into metal molds at a relatively low pouring temperature.

Figure 10: Section of a cast silver ingot showing internal cavity (pipe) and grain structure.

When metals solidify, they shrink, simply because the atoms pack closer together. For example, gold alloys contract by about 5% by volume on solidification. This is usually evident as a shrinkage cavity on the top of an ingot or casting, as we see schematically in the previous figures, and it may be necessary to provide a reservoir of molten metal to allow for this shrinkage, as we do in the central sprue of an investment casting tree. Sometimes, the top of the casting can solidify prematurely, leaving molten metal inside which will also shrink on solidification, leading to internal porosity or a 'pipe' as it is known. Figure 10 shows a vertical cross-section of an ingot of silver, illustrating the internal porosity towards the top due to this effect. Note the grain structure of columnar and equiaxed grains, like that of Figure 9.

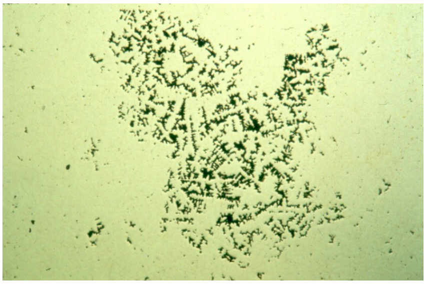


Figure 11: Shrinkage pore in an 18K yellow gold investment casting. The dendritic structure is evident here.

In a similar way, molten metal can become used up between dendrite arms as they grow during solidification and so it is important to feed more molten metal back into this region to allow for the shrinkage on solidification. This becomes increasingly difficult for alloys with a wide solidification range and with certain shapes of casting. Failure to provide adequate feeding of metal will give rise to shrinkage porosity, which can markedly reduce strength of the casting (for example, fracture of prongs in castings is often due to such shrinkage porosity). This is particularly a problem in investment casting of jewelry. Figure 11 shows a shrinkage pore in a gold casting at high magnification. The growing dendrites can be clearly seen and, as no liquid metal was available to feed this area to take up the shrinkage on solidification, so porosity resulted.

REFINING CAST MICROSTRUCTURES BY WORKING

As we have seen, cast microstructures may not be optimum for manufacturing or service. Chemical segregation ('coring') and coarse structures can lead to poor mechanical and corrosion properties. So. working of ingot material serves two purposes: (a) to change the physical shape to that desired (sheet, rod, wire, etc) and (b) to refine the structure. This may involve breaking down coarse grain structures, reducing segregation and refining coarse second phases to smaller, more uniformly distributed ones.

Much of this is best achieved by hot working the material, by hot forging or rolling, extrusion and/or drawing or combinations of methods. This will refine the structure but leave it in a soft annealed condition. In hot working, as the metal deforms, it is at a high enough temperature for it to recrystallize (anneal) during the deformation.

If we wish to impart additional hardness and improved strength as well as a more accurate shape and superior surface, then we cold work the material, usually at ambient temperature. Here the temperature is insufficient to promote annealing. This increase in strength and hardness that results is called work hardening

As I discussed last year, if we overwork a material, it can crack or fracture, so we need to anneal the hard worked material from time to time to restore the soft, ductile condition and enable further working. Annealing involves a process of recrystallization, where the hard deformed grains reform themselves into new undeformed grains by a nucleation and growth process analogous to that described for solidification.

Before working ingot materials, we often need to grind off surface defects and crop off the top of the ingot containing the pipe to prevent defects such as surface cracks, oxide/slag inclusions and internal cracking and porosity developing.

DEFORMING METALS AND RESTORING DUCTILITY BY ANNEALING

Ductility (or malleability or workability) is also reduced as we work a metal or alloy and, if we overwork a metal, we know from experience that it will crack and break (or fracture). When we are working metals, we know that we need to anneal them from time to time at a high temperature to restore a soft ductile condition and enable us to further work the metal without risk of fracture. What happens when we anneal to cause this restoration of ductility?

Firstly, as noted above, I should make clear that there are two types of deformation (or working) that we can impart to metals and alloys. Cold work is where we deform the material at temperatures below which the metal can self-anneal. Typically, we deform at room temperature. Hot work is done at higher temperatures where recovery (annealing) can occur during the working process. At such temperatures, the material is softer and easier to deform, and we can work the material much more heavily without fear of significant work hardening and fracture. [Note: For low melting metals such as lead, deforming at room temperature is actually hot working the metal!]

Annealing of cold-worked metals and recrystallization: The annealing process requires the heating of the deformed metal above a certain temperature for a period of time. As a result, the original alloy ductility is recovered. We can now work it further. How is this achieved? Well, annealing involves a process of microstructural change that is known as recrystallization. New, undeformed crystals (grains) grow in place of the old, deformed crystals that are full of crystal imperfections - called dislocations. The driving force for this process is a reduction in stored energy due to the dislocations. The amount of deformation (cold work) and the annealing conditions influence the crystal (or grain) size that results. We prefer to anneal more heavily deformed material to obtain a finer recrystallized grain size.

Figure 12 shows schematically what happens when we heat up cold-worked metals. As we heat cold-worked material, the temperature rises and we see that hardness/ strength (orange line) does not change much until we reach a critical temperature, when suddenly the hardness/strength starts to drop quickly as temperature increases. Along the bottom of the diagram, we can see the cold worked microstructure of the alloy (on the left). It is difficult to distinguish the individual crystals or grains. As the temperature reaches the critical temperature and the hardness suddenly falls, we can see that tiny new crystals are forming in the microstructure and, given sufficient time, they will entirely consume the worked material to give a totally recrystallized structure of new, undeformed grains. This process is called recrystallization and we have restored a soft ductile condition to the metal. We can see the ductility curve (yellow line) as a mirror image of the hardness curve. A typical recrystallized microstructure is shown in Figure 3(b). We note some grains show the presence of twins, so-called annealing twins. Annealing twins are formed because of growth accidents during the recrystallisation of deformed cubic-close packed metals; either side of a twin boundary is a mirror image of the other in terms of the crystal orientation. We should note that there is a minimum amount of cold work necessary for recrystallization to occur, typically about 12-15% reduction.

We also note that if we continue to raise the temperature, the hardness/strength continues to fall, but more gradually and the ductility reaches a maximum and starts to fall again. This is because we are growing the crystals to a larger size, as shown at the bottom right. This we prefer not to do as it can cause problems such as an 'Orange peel' surface if we bend or stamp the metal further, as illustrated in Figure 13 of stamping a ring. The outer surface appears rough, like orange peel. This is because each large grain deforms differently to accommodate the shape change, because they are oriented in different directions, giving an uneven surface. Small grains (crystals) do not show such big surface roughness.

The recrystallization process in cold-worked metals depends on several factors:

- Increased amounts of cold work make the process easier, reducing the temperature and/or time necessary.
- Increasing the temperature speeds up the process, so reducing the time to complete the process.

So, time and temperature are interdependent. For preference, we prefer to keep the temperature lower and extend the time, as it gives us more control. It is more difficult to do this if we are annealing with a gas torch, where temperatures are higher and so annealing times are short. It is easy to over anneal and get a coarse recrystallized grain size.

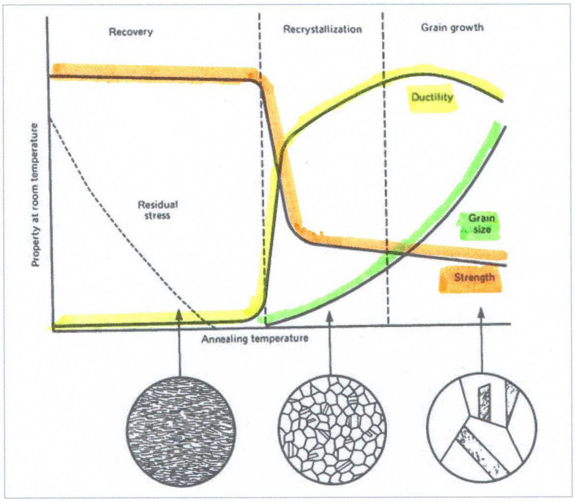


Figure 12: Recrystallization: The effect of annealing temperature on the microstructure of cold-worked (single phase) alloys

Figure 13: 'Orange peel' surface on a gold alloy ring (Courtesy U Klotz).

Alloy composition also affects the necessary temperature for recrystallization as shown in Table 1. For those who measure temperature by the color of the hot metal, the corresponding heat colors are given. We note that pure gold can recrystallize at very low temperatures and that 14 karat golds and white golds need higher temperatures.

When we anneal 18 and lower karatage gold alloys containing copper, we often find that, if we allow the hot metal to slow cool in air, it is not as soft and ductile as when we cool rapidly by quenching into water, as illustrated in Table 2. The difference in hardness increases as copper content increases. Slow cooled annealed golds are not as ductile. If we wish to further work the gold, we must water quench it. Why is this? What is happening?

Table 1: Typical annealing temperatures

Alloy	Annealing temperature °C/°F	Color
Pure gold, 24 karat	200/ 390	Black heat
21 - 22 karat	550 – 600/ 1020 – 1110	Very dark red
18 karat	550 - 600 / 1020 – 1110	Very dark red
14 karat	650/ 1200	Dark red
White gold (palladium)	650 – 700/ 1200 – 1290	Dull cherry red
White gold (nickel)	700 - 750/ 1290 – 1380	Cherry red
Sterling silver	600 – 650/ 1110 - 1200	Dark red
950 Platinum	800/ 1470	Bright red
950 Palladium	770 - 800/1420 -1470	Bright red

Well, below about 400°C/ 750°F in copper-containing karat golds at 18K and lower, it is difficult for the gold crystal lattice to retain all the copper dissolved in it. So, some copper is ejected from the crystal lattice in the solid state and forms precipitates of a second, copper-rich phase within the crystals and at the crystal boundaries. In gold-copper binary alloys, another phase change can occur at similar temperatures[1]. The solid solution phase changes to an 'ordered' intermetallic phase where the atoms of gold and copper sit in alternate layers; the crystal structure distorts to becomes face centred tetragonal (FCT) consequently. Such ordered structures are harder and stronger and less ductile. However, if we water quench after annealing, there is not enough time for the copper to be ejected or for the order-disorder transition to occur and we retain the high temperature single-phase structure, which is ductile. This allows us to further work the material.

This problem does not occur in high karat - 21 and 22 K – golds, which remain single phase down to room temperature.

Table 2: Effect of Cooling Rate on 18 Karat Golds after Annealing at 650°C (1200°F)

Composition, wt%			Hardness, HV	
Gold	Silver	Copper	Slow cooled in air	Water quenched
75	25	-	56	56
75	22	3	90	88
75	17	8	138	136
75	12.5	12.5	160	160
75	8	17	170	165
75	3	22	196	177
75	-	25	242	188

COLD WORKING AND ANNEALING: INFLUENCE ON MICROSTRUCTURE

Cold working of metals results in an overall shape change. This is reflected by a change in the microstructure, where the grains must deform to accommodate the shape change. This is shown schematically in Figure 14 for reduction by rolling. To achieve this, planes of atoms in each grain (crystal) must slide over each other, Figure 15, and this is facilitated by crystal defects called dislocations, Figure 16. Such sliding occurs over several different crystal planes in a complex way and the number of dislocations within each deformed grain grows with increasing deformation (strain). This gives rise to characteristic deformation bands within the grains, Figure 17.

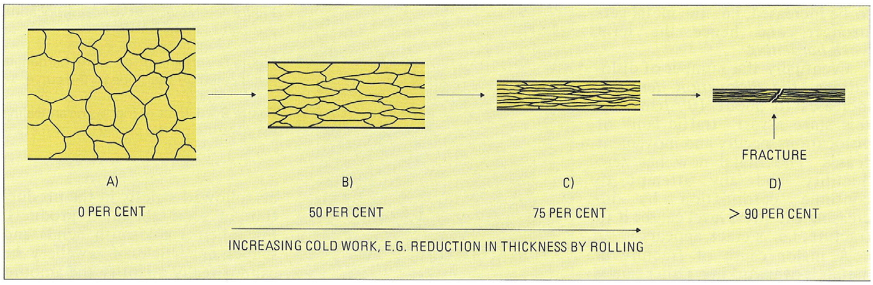


Figure 14: The effect of cold working on the microstructure of single-phase alloys

We also see this deformation in the overall macrostructure: Figure 18 shows one-half of the cross-section of a washer in the process of being upset into a wedding band; the heterogeneity of deformation is evident in its fibrous appearance. Most cold-working processes result in uneven deformation through the cross-section. In rolling or extrusion, for example, most deformation occurs at the surface, especially if only small reductions per pass are imposed. Uneven deformation can give rise to initiation of cracking from the surface, as Battaini has explained[10]. Such non-uniform deformation can also have repercussions on the grain structure on subsequent annealing when the process of recrystallization takes place. Recrystallization results in new undeformed grains replacing the old, deformed grains. The fibrous cold-worked structure is replaced by recrystallized new grains, as can be seen in Figure 19.

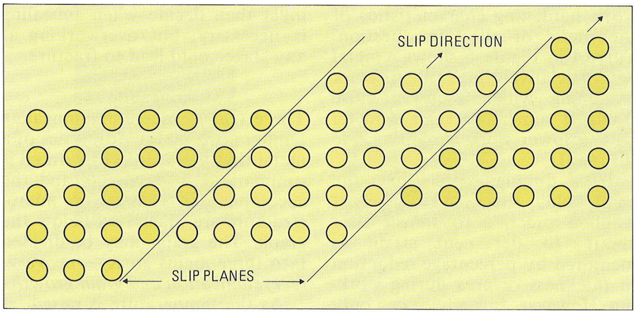


Figure 15: Simplified sketch of slip in a crystal lattice

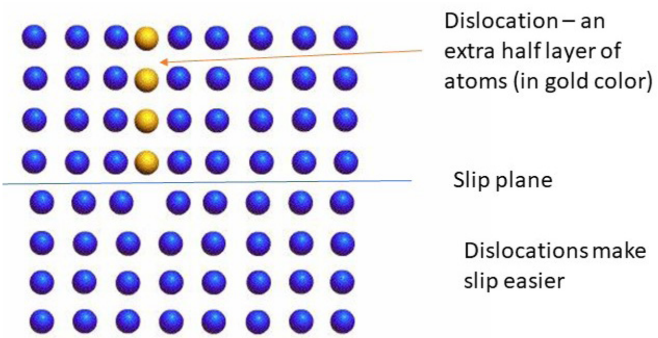


Figure 16: Schematic: A dislocation (crystal defect) in a crystal lattice

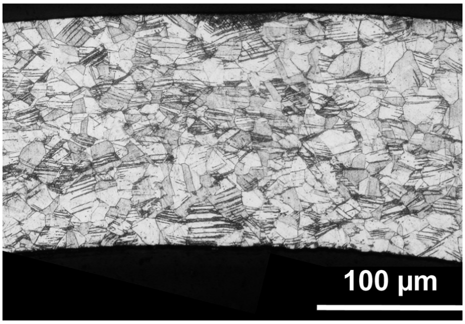


Figure 17: Deformation bands within grains after cold working: 2N yellow 18K gold tube, transverse section (from reference 10)

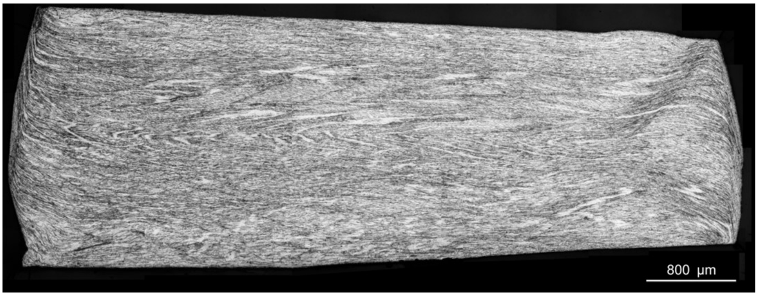


Figure 18: Macrostructure of cross-section of a nickel white gold washer after partial upsetting towards make a wedding band (from reference 10)

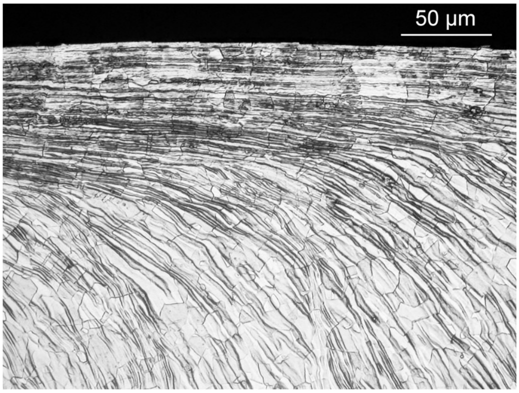


Figure 19: Recrystallized grains breaking up the fibrous cold-worked structure of washer in Figure 18 (from reference 10)

The resulting grain size after annealing depends on the amount of cold work, the annealing temperature and time. The more cold work imposed, the finer is the grain size. Annealing of material only cold-worked a small amount can result in large grains, which is undesirable (there is a critical minimum amount of cold-work necessary to initiate recrystallization, typically about 12-15% reduction). That is why annealing is often recommended only after substantial cold work, e.g. 60% reduction in thickness. The annealing temperature and time also play a part. Figure 20 shows a matrix of temperature and time of annealing for a 2N pale yellow 18 karat gold (cold-worked 70% reduction by rolling) and their effect on resulting annealed grain size[11].

The variation in annealed grain size due to uneven amounts of deformation can be seen in Figure 21 which shows part of a cross-section of a 'C' shaped wire in an annealed 18 karat nickel white gold. The inside of the flange has a finer grain size and the outer regions

CORTI

have a coarser size, reflecting the uneven amount of deformation during rolling[10]. This may not be important in some instances, but it can be in others. Orange peel surfaces and cracking may result on further working, for example, where large grains are at the surface regions, as discussed earlier.

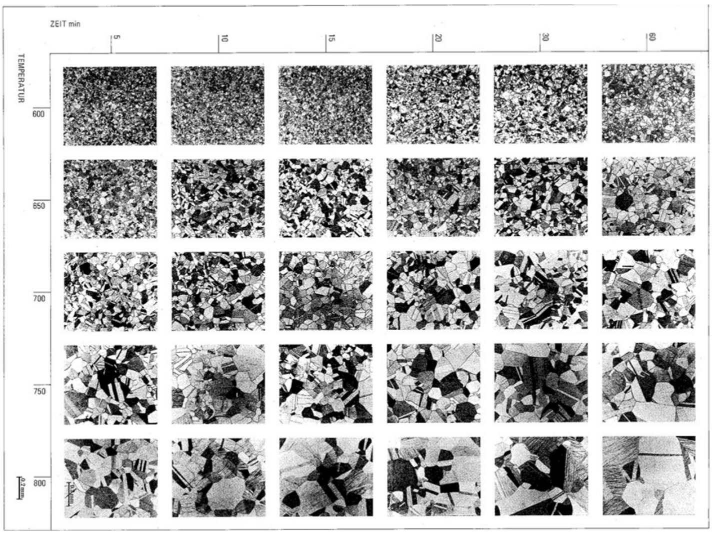


Figure 20: Effect of temperature (horizontal axis) and time (vertical axis) on recrystallized grain size of a 2N 18K yellow gold (from reference 11)

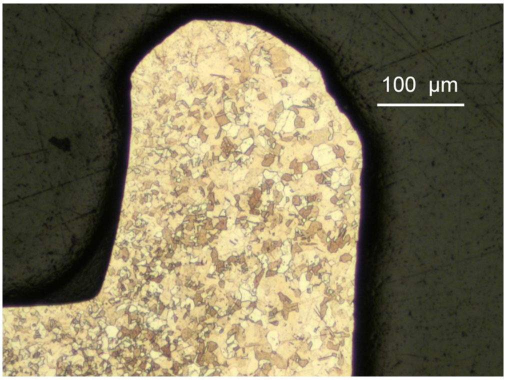


Figure 21: Grain size variation in annealed cross-section of 'C' shaped cold rolled wire in 18 karat nickel white gold (from reference 10)

SOME EXAMPLES OF MICROSTRUCTURES

To conclude this paper, it is instructive to look at some typical microstructures that one might encounter in jewelry alloys.

1. Cast structures

In many cast materials, the dendritic structure is often evident within the grain structure. A good example of this is shown for a 950 palladium alloy in Figure 22. The different orientation of each crystal nucleus is reflected in the different directions of growth of each dendrite seen within each grain due to coring. We also note that the grain boundaries are wavy, whereas annealed materials tend to have straight-sided grains.

Figure 22: As cast structure of a 950 palladium alloy

According to the silver-copper phase diagram (see Fig 9 in Part 1, reference 1), sterling silver at 7.5% copper should comprise grains of silver-rich alpha phase, from which a small amount of copper-rich beta phase should precipitate as it cools after solidification. In practice, because of non-equilibrium cooling conditions, some eutectic liquid is present on solidification and we find a microstructure comprising primary dendrites of alpha phase surrounded by a eutectic mixture of alpha and beta phases, as shown in Figure 23.

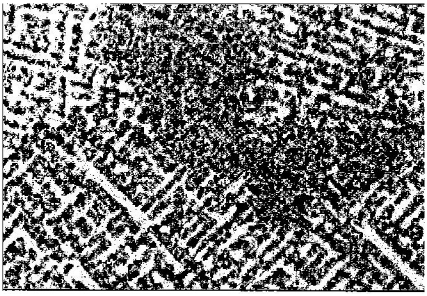


Figure 23: Cast sterling silver showing non-equilibrium microstructure of primary dendrites of α phase surrounded by eutectic $\alpha + \beta$

An alloy of eutectic composition, as is found in the silver-copper system, will comprise a eutectic mixture of the 2 phases, Figure 24. Where we have a composition clearly in a 2-phase region, as we find beyond the eutectic composition, we do see the classic cast structure, Figure 25, comprising in this instance of primary dendrites of copper-rich beta phase surrounded by a eutectic mixture of the two phases. Working such structures will refine the structure but it will still comprise grains of beta and eutectic mixture.

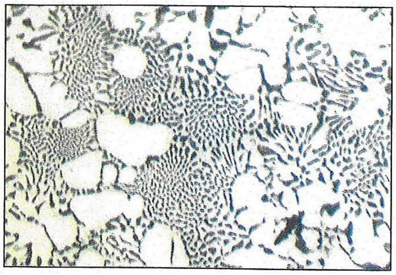


Figure 24: Microstructure of a cast silver-copper eutectic alloy composition

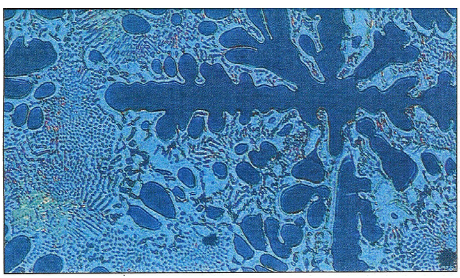


Figure 25: Microstructure of a cast copper-rich silver-copper alloy showing primary dendrites of β phase plus eutectic $\alpha + \beta$

2. Two phase alloys

Many jewelry alloys are single phase, but some comprise two or more phases. A good example is the karat golds, where the 2 phase region seen in the silver-copper system intrudes into the ternary gold-silver-copper system up to 18 karats. Thus, some karat gold alloys are two phase and are more difficult to work as a consequence; 14 karat golds are notable in this respect and zinc additions are often made to contract the 2 phase region and make such alloys more malleable (as discussed in Part 1 last year[1]). Figure 26 shows the 2 phase character of a pale yellow 14 karat gold. The primary alpha (α) phase has partially decomposed into a lamellar structure of α_1 and α_2 phases. Note the high magnification necessary to distinguish these phases.

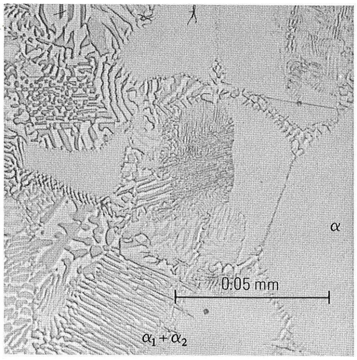


Figure 26: Microstructure of a 14K yellow gold in which the primary α phase has partially decomposed into a lamellar mixture of $\alpha_1 + \alpha_2$ (from reference 12)

CORTI

Another example is shown in Figure 27 of a complex gold alloy comprising gold, palladium, silver, tin and other metals. The matrix is a gold-palladium-silver solid solution containing islands of lamellar palladium-silver-tin phase. One can also see other darker phases between the primary matrix grains

Sometimes, second phases are due to impurities and can cause embrittlement. Battaini[10] showed the presence of silicon at grain boundaries in a 950 palladium alloy at the Santa Fe Symposium in 2007, Figure 28. Other forms of contamination include inclusions of oxides that get drawn out on cold working; Figure 29 shows a nickel white gold in which oxide inclusions have been elongated into lines of particles that can act as stress raisers and initiate cracks.

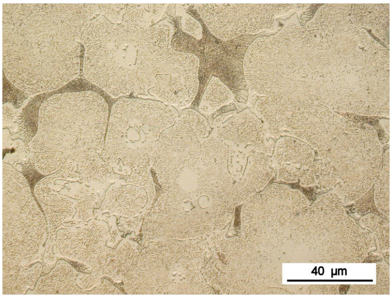


Figure 27: Microstructure of a gold-palladium-silver-tin alloy showing matrix of gold-palladium-silver solid solution and islands of a lamellar palladium-silver-tin phase (courtesy P. Battaini)

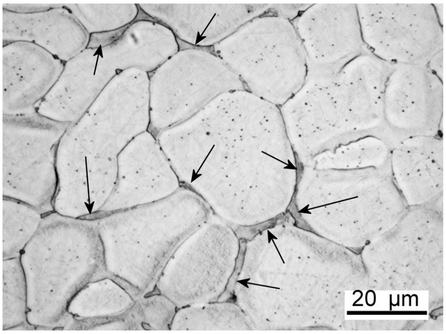


Figure 28: Microstructure of a 950 palladium alloy showing embrittling silicon phase at grain boundaries (from reference 10)

CORTI

Certain alloys depend on heat treatment to improve hardness and strength. This is known as age-hardening and this was discussed in depth in my Basic Metallurgy – Part V presentation[12] in 2015. During the precipitation stage, second phases are precipitated out within the grains as fine dispersions. These hinder slip and cause strengthening. A good example of such alloys are the high karat micro-alloys, Figure 29, in which a fine dispersion of precipitates can be seen uniformly dispersed within the grains.

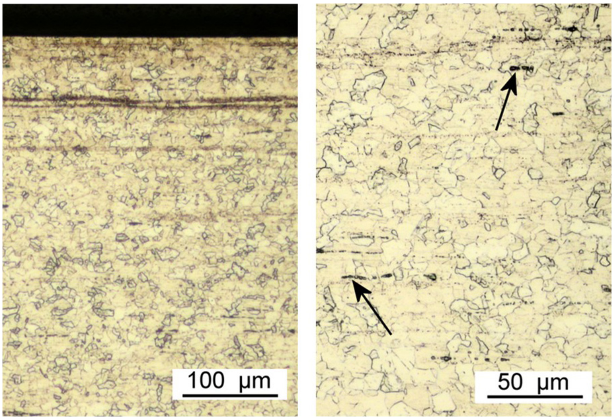


Figure 29: SEM Micrographs of longitudinal section of wire in nickel white gold showing lines of oxide inclusions within microstructure (from reference 10)

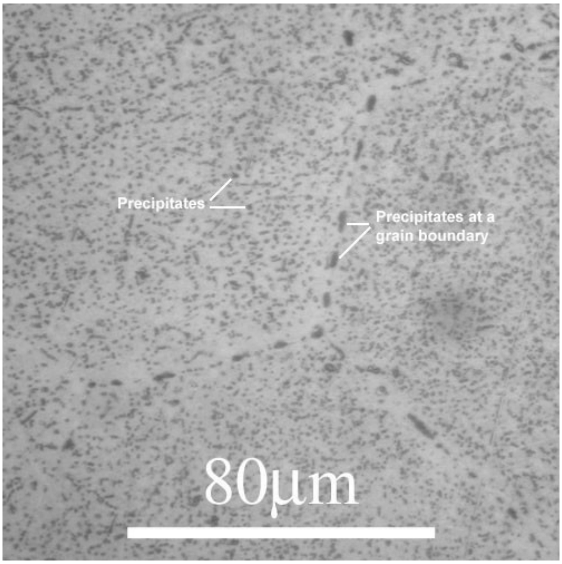


Figure 30: Microstructure of a micro-alloyed 24 karat gold, showing uniform dispersion of second phase precipitates within grains. These result in hardening of the alloy (courtesy John Bernadin)

CORTI

CONCLUSIONS

In this second part of my 'Basic Metallurgy' presentation, I have focused on alloy microstructure and the importance of controlling it, particularly grain size, in order to optimise properties of importance in manufacture and in service performance. Such control over microstructure can be exercised during solidification and in subsequent working, annealing and heat treatment.

ACKNOWLEDGEMENTS

I would like to thank many friends and colleagues in the industry for generously supplying me with photographs and information, especially the late Paulo Battaini and late Mark Grimwade.

I also thank The Jewelry Symposium team for inviting me to present and for their hospitality. Many of the figures have been taken from articles in Aurum and Gold Technology journals or have appeared in Santa Fe Symposium papers.

REFERENCES

1. Christopher W. Corti, "Basic Metallurgy of the Precious Metals – Part 1", presented at *The Jewelry Symposium*, Minneapolis, May 2023. Also, in *The Santa Fe Symposium on Jewelry Manufacturing Technology 2017*, ed Eddie Bell *et al* (Albuquerque: Met-Chem Research, 2017), 25-61.

2. Owain Houghton, Lisa Schmitt, Ulrich Klotz and A L Greer, "Will they work? A proof-of-concept study comparing a 500 Pd BMG and crystalline alloys for watches and jewelry", presented at *The Jewelry Symposium*, Minneapolis, May 2023.

3. Boonrat Lohwongwatana, "Liquid Metal – Hard 18K and 850 Pt Alloys that can be processed like plastics or blown like Glass", in *The Santa Fe Symposium on Jewelry Manufacturing Technology 2007,* ed Eddie Bell (Albuquerque: Met-Chem Research, 2007):289-304

4. Roy W.E. Rushforth, unpublished work, Johnson Matthey plc, 1978

5. Stewart Grice, "Know your defects: The Benefits of understanding Jewelry Manufacturing Problems", in *The Santa Fe Symposium on Jewelry Manufacturing Technology 2007*, ed Eddie Bell (Albuquerque: Met-Chem Research, 2007), 173-212

6. Greg Normandeau, "Applications of the Scanning Electron Microscope for Jewelry Manufacturing", in *The Santa Fe Symposium on Jewelry Manufacturing Technology 2004*, ed Eddie Bell (Albuquerque: Met-Chem Research, 2004), 345-388

7. Mark Grimwade, "The Nature of Metals and Alloys" in *The Santa Fe Symposium on Jewelry Manufacturing Technology 2001*, ed Eddie Bell (Albuquerque: Met-Chem Research, 2001), 151-179.

8. Mark Grimwade, "A Plaim Man's Guide to Alloy Phase Diagrams: Their Use in Jewellery Manufacture – Part 1", *Gold Technology* no 29, Summer 2000, 2-15. *The author (Corti) can supply a pdf file of this on request*

9. John McCloskey, "Microsegregation in Pt-Co and Pt-Ru jewelry alloys", in *The Santa Fe Symposium on Jewelry Manufacturing Technology 2006*, ed Eddie Bell (Albuquerque: Met-Chem Research, 2006): 363-376

10. Paulo Battaini, "Metallography in Jewlry Fabrication: How to avoid problems and improve Quality", in *The Santa Fe Symposium on Jewelry Manufacturing Technology 2007*, ed Eddie Bell (Albuquerque: Met-Chem Research, 2007): 31-66

11. Christian P.Susz, "Recrystallization in 18 carat gold alloys", *Aurum* no 2, 1980, 11-14 *The author (Corti) can supply a pdf file of this on request*

12. Christian P.Susz, M.Linker, P.Orosz & D.Sapey, "Heat Treatment of 14 Carat Gold Alloys", *Aurum* No 11, 1982, 17-25 *The author (Corti) can supply a pdf file of this on request*

13. Christopher W Corti, "Basic Metallurgy, Part V: Improving the properties by heat treatment", in *The Santa Fe Symposium on Jewelry Manufacturing Technology 2015*, ed E Bell *et al* (Albuquerque: Met-Chem Research, 2015), 45-66

List of Figures

CORTI

List of Tables

Table 1: Typical annealing temperatures

Alloy	Annealing temperature °C/°F	Color
Pure gold, 24 karat	200/ 390	Black heat
21 - 22 karat	550 – 600/ 1020 – 1110	Very dark red
18 karat	550 - 600 / 1020 – 1110	Very dark red
14 karat	650/ 1200	Dark red
White gold (palladium)	650 – 700/ 1200 – 1290	Dull cherry red
White gold (nickel)	700 - 750/ 1290 – 1380	Cherry red
Sterling silver	600 – 650/ 1110 - 1200	Dark red
950 Platinum	800/ 1470	Bright red
950 Palladium	770 - 800/1420 -1470	Bright red

Table 2: Effect of Cooling Rate on 18 Karat Golds after Annealing at 650°C (1200°F)

Composition, wt%			Hardness, HV	
Gold	Silver	Copper	Slow cooled in air	Water quenched
75	25	-	56	56
75	22	3	90	88
75	17	8	138	136
75	12.5	12.5	160	160
75	8	17	170	165
75	3	22	196	177
75	-	25	242	188