BASIC METALLURGY OF THE PRECIOUS METALS: PART III - CRACKS AND OTHER DEFECTS - THEIR CAUSES AND PREVENTION

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INTRODUCTION

In Part I, the effect of alloying on the various properties of the jewelry precious metals and their alloys was examined and the influence of working and annealing on properties was also explained.[1] The importance of alloy microstructure, particularly grain size, and the way it can be influenced and controlled through casting, working and thermal treatments was examined in Part II.[2] We noted that properties, alloy composition and microstructure are all interrelated. Hopefully, most of you now have a basic understanding of the metallurgy of the precious metal alloys used in jewelry manufacture and how you can exploit them to advantage.

In this third part, it is useful to look at what can go wrong during jewelry manufacture, and even beyond that when the jewelry is in service, and the causes of such defects and cracks. As we shall see, much of it is preventable through good practice and procedures, but nevertheless, even in the best of workshops, such cracks and defects do occur from time to time and can be a cause of much anguish. Even the most expert of casters succumb to incidences of incomplete fill and porosity in their castings occasionally. Frequently, whilst the nature of the defect or crack is obvious, the cause is not. There can be several causes of porosity and poor surfaces in castings and.for the occurrence of cracks in castings and wrought pieces. Such cracking is usually intergranular in nature and of similar appearance.

Whilst understanding such problems is technically interesting for some of us, porosity, cracks and other defects do have undesirable consequences for the manufacturer. These include:

- Item is unusable and unrepairable, leading to scrapping of item or even the complete batch

- There is a cost of repair or replacement of item (or batch) with new material
- Time is lost in meeting customer order
- There may be a loss of reputation and future business with customer
- There will be a concern over re-occurrence of the problem in future batches, if the cause is not understood and remedied. Such re-occurrence is unpredictable and can happen at random

In the company I formerly worked, deoxidation of silver and blistering of sheet was a continual but intermittent problem that caused a lot of headaches for the metallurgists to solve, often resulting in changes to practice, only for the problem to re-appear again some months later. Sometimes, it came and went all on its own accord. I am sure many of us have experienced such problems. Porosity & other defects in castings can come and go at random too.

In this presentation, much of what I say will focus on gold, simply because cracking and defects are, perhaps, better documented (for example, references 3-6), but much of what I say applies equally to the white precious metals – silver, platinum and palladium – and I will endeavor to give examples where I can. As previously, I will draw on examples from previous literature, including those papers presented at earlier Santa Fe Symposia. My thanks to those who have allowed me to use their pictures.

Cracking and other defects are not peculiar to the jewelry industry. They happen in all industries and in all metals and alloys. The all welded construction of Liberty ships during and after World War II was seen as a technical advance over the riveted construction of earlier times but it gave rise to some spectacular failures due to the brittle nature of the steel, when below a critical temperature. Many ships and lives were lost, especially in service in the cold North Atlantic. We now understand the problem of the ductile/brittle transition temperature and such failures do not occur anymore as we use improved steel grades that are not so brittle.

CRACKING

Cracking of jewelry materials can occur during and post manufacture. A problem is that cracking in jewelry materials is usually intergranular in nature (cracks grow around the grains along the boundaries), but the cause can vary widely, making tracing the cause difficult. Cracks can be due to several causes, including:

1. Mechanical overworking
2. Embrittlement by impurities, including gases
3. Casting and working defects and inclusions
4. Stress corrosion cracking
5. Quench cracking in castings
6. Fire cracking

Failure by fatigue and creep stresses, commonly found in stressed engineering components, are rare in jewelry and are not considered here.

Why do jewelry materials crack? The answer is simply that the imposed stresses exceed the mechanical strength of the material which may be reduced from the. anticipated value for several reasons. In this situation, the material cannot deform to relieve the stress and so it simply cracks and fractures.

Some of the various causes of cracking during casting or working and manufacturing operations can be attributed to the following factors:

- Poor quality start materials, including recycled scrap, leading to contamination, dissolved gas and possible embrittlement
- Poor melting practice, leading to casting defects such as pipes and/or gas porosity and blisters, incorporation of inclusions, excessive shrinkage porosity and chemical segregation
- Poor ingot or material working practice; this may be related to changing the alloy composition without changing the working procedure. It can also lead to surface defects such as laps that later develop into cracks.
- Incorrect annealing practice, often due to incomplete metallurgical knowledge of the precious metals and their alloys
- Residual (internal) stress, possibly linked to a corrosive environment. This can be generated mechanically or thermally and lead to phenomena such as stress corrosion cracking, quench cracking and fire cracking.

Let us look at each of the factors that can cause cracking and other defects such as porosity in casting:

1. Mechanical Overworking

This is, perhaps, the easiest cause to understand. As we know, as one works a piece of metal, i.e. plastically deforms it to change its shape, it gets harder and to further work it requires more force. This is called work hardening and results in the crystal defects – dislocations - multiplying considerably, hence increasing the resistance to further slip of the crystal planes. However, as one increases the amount of work imposed, the residual ductility decreases to the point where cracks initiate and fracture occurs, Figure 1. This is overworking the metal and, as we discussed in Part 2, it is necessary to anneal our metal before one reaches this point to restore ductility and allow further working.

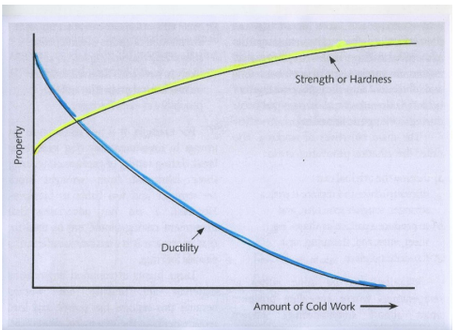

Figure 1: Effect of working on properties (Grimwade[8])

It is worth recalling that all metals and alloys (with rare exceptions) are composed of many crystals (or 'grains'), where the atoms are arranged in a regular array called the crystal lattice. They are 'polycrystalline' and, during deformation, each crystal must change its shape to accommodate the overall shape change.[2,7] It does this by a process of slip whereby the crystal planes slide over each other in a complex way via lattice defects called dislocations. At the surface, the movement of crystal planes can lead, at the microscopic scale, to intrusions and protrusions and these can also act as nucleation sites for surface crack initiation. It is also worth noting that hard particles such as inclusions or second phases at the surface, Figure 2, or within the alloy can act as stress raisers, i.e. they amplify the local stresses in the adjacent metal, which means that cracks can initiate and grow more easily around them, even when the imposed stresses are lower than those normally leading to crack formation.

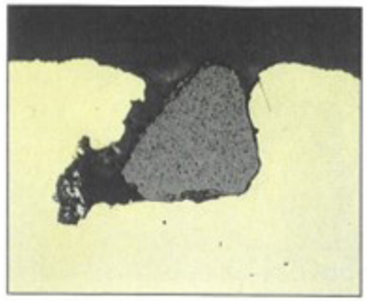

Figure 2: Inclusion at surface of casting (Ott[3])

2. Embrittlement

Certain impurities and alloying metals can cause embrittlement in all precious metals at low concentrations. This means the material has less inherent ductility and will fail prematurely under moderate stress at room or at hot working temperatures. The latter is often called 'hot shortness' and results from incipient melting of the grain boundary phases at the working temperature. Typical embrittling elements are listed in Table 1.

Table 1: Typical impurities that lead to embrittlement and hot shortness in the precious metals

Precious Metal	Impurity
Silver (Ag)	P, Pb, S, Se, Si, Te
Gold (Au)	P, Pb, S, Si, Bi
Platinum (Pt)	C, P, Pb, S, Si
Palladium (Pd)	C, H, Pb, S, Si

C –carbon, Bi – bismuth, H – hydrogen, P –phosphorus, Pb – lead, S – sulfur, Si – silicon, Se – selenium, Te – tellurium

Many of these impurities are low melting point elements and, if present in the metal, tend to lie preferentially on the grain boundaries. Many of the low melting point metals used in solder compositions to lower the melting point of the alloy, such as tin, indium and zinc, can also cause embrittlement at higher concentrations. Embrittlement by low melting point elements tends to result from the formation of low melting point metallic second phases or eutectics, either the contaminating element itself, which has extremely low solubility in the alloy, or a reaction product of the contaminant with gold, silver or copper in the case of karat golds or with platinum or palladium. These are often

CORTI

intermetallic phases which in themselves are usually brittle. Table 2 illustrates the low melting points of some eutectic systems that can be formed. Reti has noted[9] that phosphorus, used as a deoxidant in sterling silver at concentrations up to 0.02%, reduces the eutectic temperature and so causes hot shortness (incipient melting) when annealing at temperatures as low as 705°C (1300°F). The eutectic temperature, according to the silver-copper phase diagram, is 779°C, some 74°C higher! I have seen catastrophic failure of a platinum crucible being used to manufacture single crystal materials for electronic applications from molten rare earth oxides. The problem was found to be due to sulfur which forms a (relatively) low melting sulfide eutectic with platinum. Someone had filled the crucible with sulfides, not oxides, of the rare earths in error.

Table 2: Eutectic melting temperatures of some contaminants in precious metals

Contaminant	Phase formed	Melting point	Comment
Si - in Ag	Eutectic	835°C	**@ 3.1% Si**
Si - in Au	Eutectic	363°C	**@ 3.2%Si**
Si - in Pt	Eutectic	~830°C	**@ ~ 5% Si**
Si - in Pd	Eutectic	824°C	**@ ~5% Si**
Pb – in Au	Eutectic	212°C	**@ 84.1% Pb**
Sb – in Au	Eutectic	360°C	**@ ~27% Sb**
Sn – in Au	Eutectic	278°C	**@20% Sn**
Ge – in Au	Eutectic	361°C	**@ 12% Ge**
Au-Ge-Si solder alloy (22 karat)	Eutectic	~370°C	See reference (11)

Au – gold, Ag – silver, Pt – platinum, Pd – palladium, Ge – germanium, Pb – lead, Sb – antimony, Si – silicon, Sn - tin

Most of the low melting point contaminants such as silicon and lead can cause embrittlement of gold, silver, platinum and palladium alloys at very low concentrations. Normandeau has quantified the embrittlement of karat golds by silicon,[10] Figure 3. The effect is magnified if the grain size of the alloy is large as these second phases tend to be dispersed as very thin films around the grain (crystal) boundaries. Fine-grained alloys will tend to have a lower concentration of embrittling phase per grain boundary area. Often, these contaminants manifest themselves as cracking during metal working operations although, as will be discussed later, there are other reasons for karat gold and other precious metal alloys failing during fabrication. An example of embrittlement by silicon in a 500-fineness palladium alloy ingot after working is shown in Figure 4. This was due to stirring the melt with a quartz rod.[12]

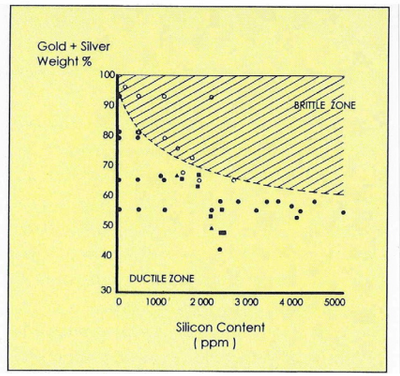

Figure 3: The influence of silicon concentration on the ductile-brittle transition in karat golds (Normandeau[10])

Figure 4: Cracking of a 500-palladium alloy ingot on working due to silicon embrittlement (Binnion[12])

2.1 Sources of Contamination

Embrittling elements can occur in alloys from several sources:

- Impure starting materials
- Impure scrap
- Pick-up during processing from the atmosphere or contact with other surfaces
- Overalloying

Starting Materials: It is essential to have good clean, oxide-free metals for making up alloys, be they the pure metals or pre-alloys (master alloys). All should be analyzed or purchased with certificates of analysis as a matter of good practice. The purity of the precious metal, be it gold, silver, platinum or palladium, should be at least 99.9% with certain impurities such as lead, tin,

bismuth, antimony, selenium and tellurium specified as less than 0.01%, all of which can be present, and which can lead to alloy embrittlement.[13-16] Gas content, especially oxygen in the case of silver and hydrogen in the case of palladium, should also be low. Eccles has highlighted contamination of pure silver by selenium and tellurium[15] when used to make tarnish-resistant Bright Silver which contains some silicon and germanium. This leads to embrittlement of castings unless Se & Te levels are below 2ppm. Embrittlement problems can also arise in karat golds from the use of free-machining brass (containing lead) as a means of adding pre-alloyed zinc (only use lead-free brass for alloying) and the use of silicon-containing master alloys. Both lead and silicon can embrittle all precious metals at low concentrations. Battaini gives an example of silicon embrittlement for a 950 palladium alloy,[6] Figure 5 which shows the silicon-rich phase sitting on the grain boundaries.

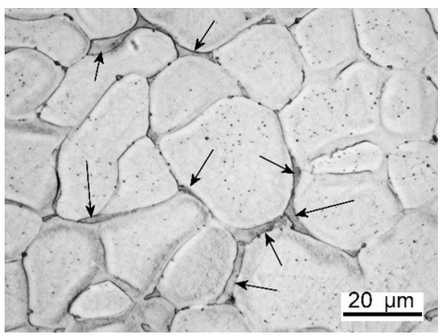

Figure 5: Silicon-rich phase sitting on grain boundaries of a 950-palladium alloy (Battaini[6])

Any attempt at working embrittled material will result in cracking as seen in Figure 4. Cracking in an 18K yellow gold due to silicon embrittlement[3] is shown in Figure 6. Embrittlement by 100 ppm phosphorus in 950 platinum-ruthenium bar stock material is described by Grice.[17]

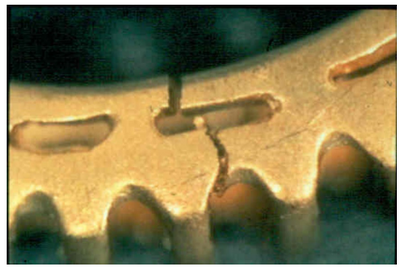

Figure 6: Cracking in an 18K red gold due to silicon embrittlement (Ott[3])

Impure scrap: However, the major problems often revolve around the use of scrap, which tends to be a continual source of contamination. This is particularly true for bought-in scrap, a common source of start material in some countries, but even internally generated scrap can be problematical, especially if it is recycled because of prior process failures. The use of scrap to make new product should be strictly controlled and, preferably, should be subject to melting and analysis before use in making up new alloy ingots or recycled in investment casting.

Typical contaminants arising in scrap include refractory materials, such as investment particles on poorly cleaned recycled sprues, oxides from dirty surfaces, silicon from casting alloys and lead-tin solder from repaired jewelry, all leading to inclusions or alloy embrittlement. Investment particles on old casting sprues can lead to sulfur contamination and to gas porosity. Any scrap jewelry containing soldered joints is likely to result in some contamination, especially if some of the newer solders containing indium, germanium or tin have been used. The only guaranteed safe way of utilising scrap is to refine it first.

Pick-Up during processing: Carbon can be picked up during melting in graphite crucibles which is a problem for palladium and platinum alloys and palladium-containing white golds in particular. Silicon crucibles can also contaminate platinum and palladium melts if melted under reducing or neutral conditions. Grice has given an example of lead pickup on 18K gold[18] during hand raising. This is discussed later. In customer service, whitening and embrittlement of karat gold and other precious metal jewelry can occur from contact with liquid mercury (usually from broken thermometers). This is a common cause, surprisingly. Mercury forms amalgams with precious metals very quickly.

Overalloying: Too frequently, melters tend to add 'a bit extra' when alloying. Very minor additions to alloys such as grain refiners and fluidity promoters (silicon) can be deleterious if too much is added[10,14] as Normandeau has shown for silicon in karat golds, Figure 3.

3. Casting and Working Defects

3.1 Melting and Casting Practice

Continuous casting of karat gold and silver alloys almost always uses high density, fine grain graphite for the die material to ensure good quality product. Continuous casting can give much higher quality and higher product yields, because there is no shrinkage pipe, as occurs with statically-cast ingots. However, erosion of the die can lead to graphite inclusions in the melt. Surface defects are also a possibility if die wear or sticking occurs to any extent but, by and large, continuously-cast materials should seldom give rise to mechanical defects. One rare example of cracks on ring surfaces after working, Figure 7, made from continuously-cast 14K gold tube, is attributed to incorrect casting conditions.[3]

Figure 7: Cracking on the surface of a ring made from continuously cast 14K gold x20 mag. (Ott[3])

Static casting of ingots tends to be a much simpler operation, with melting by gas heating, oil-fired furnaces, electric resistance heating or, preferably, induction heating which ensures maximum stirring of the alloy constituents, although physical stirring of the melt with graphite or refractory rods is commonplace. For gold and silver, crucibles are typically clay-graphite or graphite (fireclay for nickel-white golds, as nickel will react with graphite) and casting will usually be into dressed iron moulds or water-cooled copper moulds. For platinum and palladium, zirconia or zirconia-washed silica crucibles are preferable. That said, many palladium casters use silica crucibles without too much problem, provided temperatures are kept to a minimum and reducing atmospheres are avoided.[19]

Static casting can be a source of several problems:

Shrinkage and pipes: When a cast ingot solidifies, it shrinks and this becomes evident as a central pipe at the top of the ingot, Figure 8. It is necessary to cut off this pipe before working the ingot, otherwise a central defect will be introduced which will elongate on working and is likely to result in subsequent longitudinal cracking. The extent of the pipe into the bulk of the ingot is increased if the casting temperature is too high and it is normal practice to restrict this temperature to no more than 200°F/95°C above the liquidus temperature of the alloy. High casting temperatures also encourage large grain sizes which decrease the ductility of the alloy[2] and, at the same time, magnify the effect of any low melting point impurities which might be present.

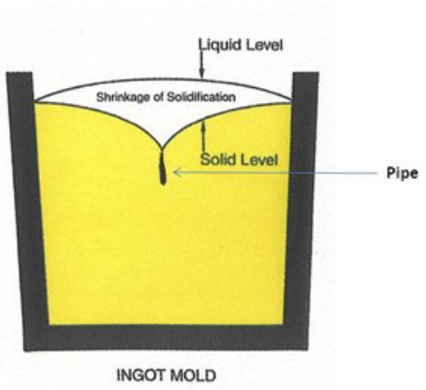

Figure 8: Schematic of pipe formation in a statically cast ingot (courtesy E. Bell)

In investment casting, shrinkage can manifest itself as shrinkage porosity, Figures 9 & 10, if feeding of liquid metal to the casting is prevented by premature solidification in thinner sections or in the feed sprue. This has been well discussed at previous Symposia and elsewhere,[3,20-22] so it will not be discussed at length here, save to say that shrinkage porosity often has a characteristic shape (dendritic). Feed sprue positioning and diameter are important to minimise its occurrence. Sprues are preferably placed on thicker sections of the casting and multi-feed sprues may be desirable to prevent shrinkage porosity and non-fill in some complex shaped castings. Modelling of the casting process may assist in preventing such porosity through optimising the casting set-up.[23,24]

Figure 9: Shrinkage porosity in investment cast 18K gold: (a) petal broken at base, (b) & (c) porosity at base of petal (Ott[3])

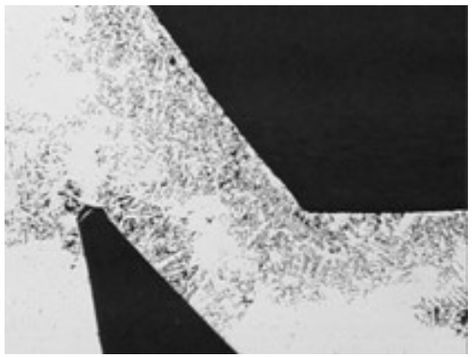

Figure 10: Shrinkage porosity in a 950 platinum-ruthenium cast ring (Grice[17])

Gas porosity and blistering: Dissolved gas in a molten alloy will be ejected as gas bubbles during solidification, due to low solubility in the solid state, and can lead to gas porosity in the casting. It is often due to sulfur dioxide, from chemical breakdown of gypsum-based investment, but can be due to oxygen, hydrogen or other gases. Typically, it is present as fine round pores, quite different in appearance from shrinkage porosity which has a dendritic shape. Gas arises from the start materials (dissolved gas or damp materials), or gas dissolved during the melting operation (aggravated by too high a melting temperature, lack of a protective atmosphere or a flux and use of gas melting). This is well documented for karat golds[3,25-29] but can also occur in the other precious metals.[30] If the gas is present in the molten alloy before casting, such gas porosity will manifest itself throughout the casting, Figure 11, whereas if it occurs as a result of chemical reaction with the investment during casting, it will manifest itself as a layer of porosity at the surface, Figure 12. Again, this

phenomenon has been well documented in the literature, e.g. by Ott,[3] and so will not be discussed in depth here. It is preventable if good practice is followed. Clean burn-out of the mold, use of cleaned scrap (especially recycled casting sprues) in the melt charge and lower casting and/or flask temperatures will reduce the probability of gas porosity. Gas porosity affects the tensile strength and ductility of castings. Ott and Raub[25] have shown a direct linear decrease in strength and ductility with increasing levels of porosity in karat golds.

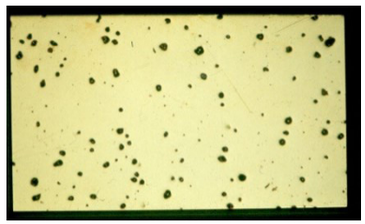

Figure 11: Gas porosity throughout the cross-section of 18K gold due to gas in the molten alloy (Ott[3])

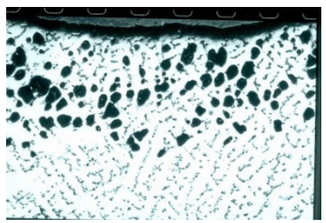

Figure 12: Gas porosity at the surface layer of 18K gold due to reaction with the investment on pouring (Ott[3])

Such porosity can show up later in fabrication operations as surface blisters or defects or cracks or as internal porosity. Silver is especially prone to this problem, arising from poor de-oxidation practice. Initial working may flatten the pores and cause small laminations and cracks, or it may close the porosity only for annealing operations to allow the gas to expand and reappear as pores and blisters on the surface. Also, annealing silver containing dissolved oxygen or copper oxide inclusions in hydrogen-containing atmospheres can result in hydrogen absorption and the formation of pores due to the 'steam' reaction between the hydrogen and oxygen[31]:

$$2H_2 + O_2 \rightarrow 2H_2O \text{ [gas]}$$

$$H_2 + Cu_2O \rightarrow 2Cu + H_2O \text{ [gas]}$$

It can also occur in karat golds. An example of surface blistering and porosity in thick sheet of 18K yellow gold, due to the steam reaction on annealing in a hydrogen-containing atmosphere, is discussed by Ott[3]. Another well-known problem with silver alloys due to gas ingress is the formation of firestain due to internal oxidation of copper (or zinc) during annealing, Figure 13. As silversmiths will know, this can be hard to polish out!

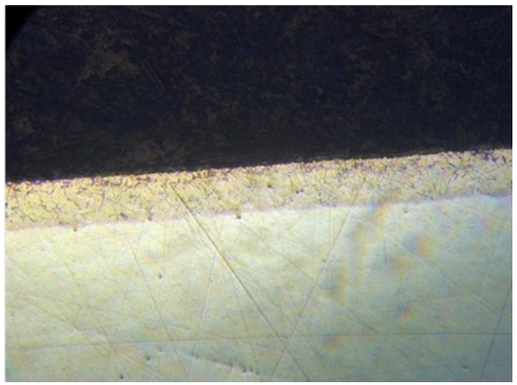

Figure 13: Firestain (subsurface internal oxidation) in sterling silver (Grimwade[32])

Inclusions: Inclusions of oxides and other refractory particles, graphite and even metallic particles can be incorporated into the melt from several sources such as erosion of the crucible surface by impacting molten metal, from spalling of furnace insulation or lining, broken stirring rods, the reaction between the atmosphere and alloying element (for example, oxygen and copper form copper oxide, zinc forms zinc oxide films) or the use of grain refiners, particularly iridium in karat golds, which have not been dispersed correctly. Such inclusions can act as stress raisers and give rise to cracks or failure during subsequent working.

Surface defects: Surface defects, which can lead to cracks, can arise due to poor melting and casting practice. These arise from solidified splashes sticking to the mold wall during casting, surface inclusions, oxidation and mechanical damage. The golden rule

should be to inspect all ingot surfaces and remove (by filing, grinding or machining off) and generally clean away all evidence of defects before any working operations are undertaken. If necessary, the surface might have to be milled to ensure it is clean and flat.

Investment (lost wax) casting: Investment (lost wax) castings are prone to (i) embrittlement, particularly where silicon-containing alloys and scraps are used, (as has been discussed above), (ii) to inclusions from crucibles, weak investment molds and unclean scrap, (iii) to quench cracking (see below) and (iv) to shrinkage and gas porosity. Large porosity, shrinkage porosity in particular, may act to cause cracking during subsequent processing.

Poor surface detail or rough, sandy surfaces and metal fins can also occur in investment castings. These are due to poor burn-out of the mold, weak molds that crack or to reaction of the molten metal with the mold material (typically gypsum). These phenomena are well documented (e.g. Ott,[3] Faccenda[22]) and have been reported at Santa Fe Symposia too.

3.2 Working Practice

Overworking: All forms of metal working - sheet and rod rolling, wire and tube drawing, blanking, stamping, coining, spinning and raising, milling, turning and machining or simply bending and hammering by hand - result in the material becoming harder and less ductile. The degree to which it hardens and loses ductility depends on the amount of deformation imparted. If material is overworked, the ductility reduces to zero and it will crack, and fracture as discussed earlier. Materials in the age-hardened condition, or with hard second phases, will have inherently lower ductility and tend to crack more easily on further working.

Therefore, at appropriate stages in the working process, the material needs to be annealed to restore its ductility (through the process of recrystallization.[2] The rate at which alloys work-harden and the extent to which they can be worked varies from alloy to alloy. Typically, most precious metal alloys can be worked up to about 70% reduction in area (strain) before requiring annealing. However, there are considerable variations: nickel white gold hardens rapidly and requires relatively small reductions per working operation with annealing necessary after perhaps only 35 or 40% reduction. On the other hand, fine gold and some of the high karat golds can be worked well in excess of 90% reduction in area before annealing becomes necessary.

Rolling: Rolling of sheet material can result in edge cracking; this is

due to overworking between anneals, exacerbated by poor quality surface on the edges. It is important to trim the edges at the time edge cracking is seen, as further rolling after annealing will increase the danger of some cracks running in towards the sheet centre, Figure 14. Fins and laps can arise during rod rolling, which can open up as cracks at later stages. The formation of fins is due to pushing too much material into the rolling groove, so that the rolls are forced apart and excess metal is squeezed out sideways, Figure 15 These fins are then rolled into the rod, becoming laps. Their formation can be prevented by avoiding too large a reduction and by rotating the rod through 90° between successive passes.

Figure 14: Schematic: Edge cracking in rolled strip (Grimwade[4])

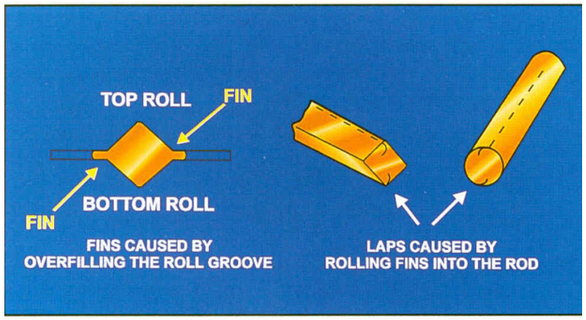

Figure 15: Schematic: Lap formation in rod rolling (Grimwade[4])

Sheet forming: Sheet metal forming operations such as stamping or deep drawing can also result in cracking due to localised overworking, Figure 16. Fracture will take place at the weakest or thinnest part and is most likely where the sheet is bent round an angle under tension as extra thinning will tend to occur there.[5] It may be necessary to part shape the component in one die-set and

then further form in another die-set. This is the basis of stamping in which strip or sheet is processed progressively in a series of dies to achieve the desired final shape. Selection of the correct material and processing conditions is important, if cracking is to be avoided.

Figure 16: Cracking due to overworking during stamping (Klotz & Grice[5])

Embrittlement by impurities:
Certain metallic impurities (including silicon) will embrittle precious metal alloys, as has been discussed in the earlier sections. Manual working, such as raising, and repair operations often involve hand working on a soft former, frequently made of lead, to prevent surface damage. An example of embrittlement has been reported by Grice[18] whereby the forming operation allowed lead contamination of the gold material surface, with diffusion of the lead into the gold on subsequent annealing or soldering and leading to embrittlement and failure of the jewelry item, Figure 17. Use of metallic lead in contact with gold and the platinum metals is always risky but, if considered essential, there must be separation of the piece from the lead by interleaving with a tough grade of paper.

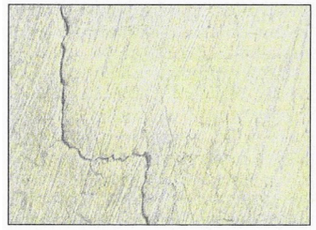

Figure 17: Cracking due to lead contamination during hand raising of a 2N 18K gold sheet (Grice[18])

Non-metallic inclusions: Hard refractory inclusions resist deformation during working and act as stress raisers, i.e. crack initiators, in the precious metal alloy. If present on the surface, they can break out, leaving large surface porosity[3] that is drawn into a longitudinal surface crack on further working.

Residual stresses: Residual or internal stress may be present in a wrought item, often due to non-uniform plastic deformation during processing,[6] for example in rod, wire and tube drawing where tensile forces may develop at the surface and compressive stresses in the central region. Such stresses can be circumferential, longitudinal or radial. They are often localised and can lead to spontaneous cracking, for example during heat treatments. Nickel white gold is particularly prone to this problem,[6,33] where it is known as fire cracking; it is discussed specifically later.

3.3 Incorrect Annealing Practice

Selection of the incorrect cooling conditions after annealing can, paradoxically, lead to hardening rather than softening in some karat golds, due to metallurgical instabilities, namely second phase formation. On subsequent working, the material cracks. Yellow-red golds in the 8-18K range should be rapidly cooled after annealing by quenching directly into water; this maintains a soft ductile condition, whereas slow cooling results in second phase formation and hardening. Repairers should also anneal and water quench such jewelry items before re-sizing or repair for this reason.

Where working of a material results in residual internal stress, subsequent annealing can lead to spontaneous cracking and the presence of a corrosive agent in the environment can lead to stress corrosion cracking at a later stage. Residual stresses can be relieved by a low temperature anneal without reducing the hardness, as discussed below.

Over-annealing (i.e. annealing at too high a temperature and/or too long a time) can result in a large, coarse grain size[2] and subsequent deformation can lead to premature cracking and fracture (as well as an 'orange peel' surface). This is particularly a problem with torch annealing, where the capability to control temperature is limited.

Quench and Fire Cracking: Nickel white golds, as any manufacturer knows, can be extremely difficult to fabricate. They tend to have a high rate of work hardening, which effectively means more frequent annealing is required and they can separate into two immiscible phases on slow cooling after annealing, which normally dictates quenching from the annealing temperature.

However, some nickel white golds and other yellow karat gold alloys, particularly those containing silicon additions are prone to quench cracking which is usually attributed to the generation of residual or internal stresses between the more rapidly cooled outer layers and the less rapidly cooled interior of the material on quenching, sufficient to result in cracking in what is an inherently brittle alloy. To avoid the quench cracking effect and also to avoid the hardening effect induced by slow cooling in nickel white golds, a variety of techniques are used to achieve an intermediate cooling rate after annealing. These include forced air cooling, cooling by placing on an iron plate, quenching into hot water or oil, or slow cooling to close to the critical temperature when precipitation of the second phase occurs and then quenching. Individual manufacturers will have their own techniques for particular alloys and sizes of component but still will often face difficulties.

In the case of investment cast silicon-containing karat golds, such quench cracking is attributed to hot shortness, whereby quenching the flask (mold) after casting from too high a temperature leads to hot tearing and cracking. This is due to low-melting silicon-rich phases on grain boundaries. Figure 18 illustrates an example of a quench crack in a 9K gold.[34] McCloskey has also reported it in 14K golds.[35]

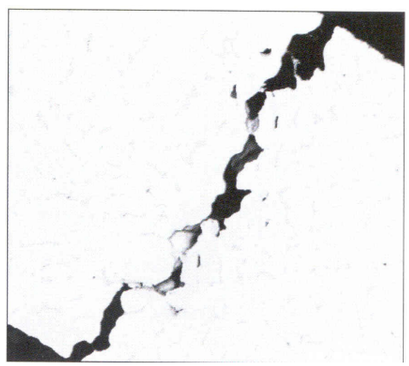

Figure 18: Quench cracking in investment cast silicon-containing 9K gold (Grice[34])

The second problem that can be faced by the fabricator is fire cracking, particularly in nickel white golds,[33] which occurs during the heating associated with annealing or soldering. The cause is

usually attributed to the presence of residual stresses from working operations, these being sufficient to fracture the component as the temperature increases (and the strength, therefore, decreases). The remedy is to heat up to 575°F/300°C slowly, possibly holding at this temperature for a time, to relieve the stresses before continuing to the annealing or soldering temperature. An example of this type of failure is shown in Figure 19. Recent research, being presented at this symposium,[43] has examined fire cracking in 18K copper-rich rose golds which is attributed to stresses induced by the ordering phase change. This work has shown that it can be mitigated by novel grain refining techniques.

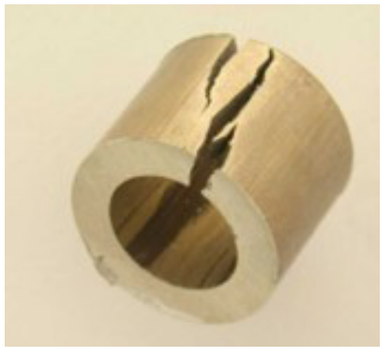

Figure 19: Fire cracking in an 18K white gold tube (Normandeau[33])

3.4 Stress Corrosion Cracking

Stress corrosion cracking can occur in some lower karat gold alloys by the combined effects of applied or residual stress and a corrosive agent, often vapours of chemicals in the local environment. Examples are not uncommon in 8, 9 and 10K golds and, less frequently, in 14K golds, particularly nickel white golds. Cracking or, as sometimes happens, spontaneous failure, only occurs in the presence of both influences and may happen during manufacture; for example, a spool of wire left exposed to fumes from a pickling shop can completely disintegrate. More worryingly, it can occur much later in jewelry owned by the customer, even after several years of satisfactory service. The mechanism of stress corrosion cracking is complex and has been discussed by Rapson, Normandeau and others.[36-41]

The residual stress may be introduced during production by the manufacturer and so all potentially susceptible alloys should be fully annealed or, at least, *stress relief annealed*. This latter is an annealing treatment at 480 – 650°F/250 – 350°C, typically for 30

mins. It has little effect on hardness or grain structure but simply relieves internal stresses. However, stresses can also be introduced in service with the customer (for example, chains stretched by children pulling on them) or by the jeweler when rings are re-sized without a subsequent annealing treatment. Initiation of a crack is likely to be at some stress raiser - a scratch or defect or even a stamped Hallmark or manufacturer's mark.

As for the corrosive part of the equation, chlorine or chlorides are a major agent; acids and pickling solutions are the usual source at the manufacturer but, for the user, the list is almost endless: detergents and household cleaning fluids, inks, swimming pool water, sea water and coastal atmospheres, some foodstuffs, perfumes, deodorants and human sweat can all act as the source of corrodant.

Figure 20: Stress corrosion cracking of a prong in a 14K gold (Grice[18])

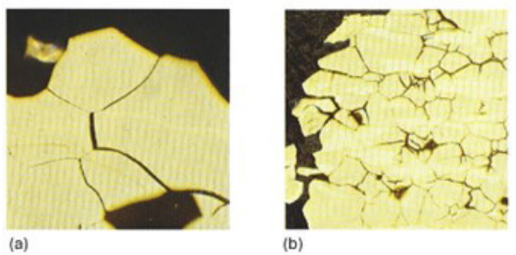

Figure 21: Stress corrosion cracking along grain boundaries in a 9K gold (a) chain link, (b) casting (Grimwade[41])

The failure usually manifests itself by a characteristic inter-granular fracture, examples of which are shown in Figures 20 & 21. The susceptibility of alloys to stress corrosion is particularly determined by composition and by metallurgical structure but the

subject is a complex one with initial attack determined by local differences in composition and initiating at a defect or stress raiser. However, despite the vulnerability of the low karat golds to this phenomenon, it is not widely observed today[42] which tends to suggest that the manufacturers at least are aware of the potential problem and take steps to minimise its occurrence.

CONCLUSIONS

The issue of cracking, porosity and other defects arising during the fabrication of precious metal jewelry, or later during service or repair, can be complex because, although there are well-defined causes, their appearance is not uniquely associated with one particular cause. To establish the precise reason for failure may require specialised equipment and knowledge, and the situation may be further complicated as, frequently, defects may arise because of more than one cause. Most cracking is intergranular in nature, for example. Incidences of porosity can look similar but arise from several causes.

However, there are probably two aspects of manufacturing that contribute most towards minimising the production of defective or scrap jewelry products:

- a good understanding of the metallurgy and processing of the precious metals and their alloys, and
- the establishment of good manufacturing practice for materials and products and the strict adherence to those practices.

All too frequently, operators on the shop floor will introduce their own "improvements" to procedures or the size or alloy composition will be changed without considering a simultaneous change in procedure. Whilst most precious metal alloys are tolerant and eminently castable and workable, some are very much more difficult to fabricate, but all of them benefit from establishing good manufacturing procedures that are always followed.

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