

WEEK 17

THE DETERIORATION OF GOLD ALLOYS AND SOME ASPECTS OF THEIR CONSERVATION

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Abstract—The different ways in which gold alloys can deteriorate are described. The principal alloys discussed are gold-copper, gold-silver and gold-copper-silver. Examples of South American gold alloys from Colombia and Panama are used to illustrate the different types of corrosive attack. Some problems related to the conservation of gold alloy antiquities are mentioned, together with the difficulty of the preservation of technological evidence.

1 Introduction

Gold in the native state, whether obtained from lode or placer deposits, usually contains appreciable amounts of silver (typically from 5% to 45% by weight), and often a little copper (about 0.1%–5%), as the major accompanying impurities. High percentages of silver, from about 40% upwards, constitute natural electrum which can be pale green or silvery in colour. This alloy could also be fabricated, of course, by the addition of extracted silver to golds containing lower impurities of silver. Copper can also be added to make a range of alloys varying from moderately debased gold, containing perhaps 5%–15% of copper, to copper containing small additions of gold (about 0.5%–5%). Small additions of gold are thought to have been included in some copper alloys to influence the surface colouring characteristics of the alloy after various forms of surface treatment [1–3].

Within this broad spectrum of gold alloys lie an important range of compositions corresponding to the gold-copper and gold-silver-copper alloys used especially in South America. The gold-copper alloys are often referred to as tumbaga alloys, the compositional data for which varies from copper contents of about 90% down to about 10%. European Bronze Age and Egyptian gold artifacts are also occasionally found to be made from fabricated gold-copper alloys [4,5], although the Old World utilization is on a limited scale compared with the many thousands of tumbaga alloy objects which are known from South America. Silver was more plentiful in the Peruvian area, and many gold alloys had deliberate additions of both silver and copper [6]. Since the gold used to make the tumbaga alloys usually contained some silver as an accompanying impurity, these alloys are also in fact ternary gold-copper-silver alloys. Alloys of gold and silver are of very

wide occurrence, both for the production of coinage and for a variety of decorative metalwork [7]. The South American gold-copper or gold-copper-silver alloys were frequently finished by a depletion gilding process [6,8] which removed the alloying constituents from the outer surfaces leaving a thin, porous layer of gold which could then be polished to create a gilded surface. The presence of these depletion gilded layers over debased gold alloys often creates severe corrosion which will be discussed in detail below.

2 Types of deterioration

It is often assumed that pure gold will not undergo any corrosion during burial, but this may not be so; it is known, for example, that biological processes may result in small concentrations of gold being accumulated by certain plants, whilst water-borne decomposing vegetable matter has been shown to deposit gold particles from solution if flowing over auriferous rocks [9]. The gold, therefore, must be taken into solution, and it is thought that both cyanogenic glucosides in plants and a variety of amino acids in micro-organisms are responsible for the dissolution of gold. A saturated solution of sodium chloride can also attack gold, as can bromides which may be present near marine environments. One would not expect serious decay of gold antiquities necessarily to arise from exposure to these types of corrosive agents, although some superficial attack of the immediate surface is certainly possible. Returning to the consideration of gold alloys, the different forms of possible deterioration can be classified as follows:

- i) Tarnishing.
- ii) Dissolution of anodic constituents.
- iii) Stress corrosion cracking and embrittlement.
- iv) Changes due to order-disorder transformations.

2.1 Tarnishing

Alloys of gold with copper or silver, or with both metals, are liable to exhibit thin films of surface corrosion which can either be derived from the deposition of metallic ions from solution (such as iron staining) or from reactions with sulphur-containing contaminants, particularly hydrogen sulphide, H_2S . It is well known that unprotected silver objects are liable to react with gaseous pollutants with the for-

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mation of grey-brown films of silver sulphide, Ag_2S . Vernon [10] found that H_2S can produce discoloration even after careful drying of the air. Very low relative humidities in themselves are therefore not enough protection if the atmosphere is contaminated. Higher relative humidities promote more severe tarnishing, although the presence of condensed water on the surface may retard the reaction. The same reactions which lead to Ag_2S formation on pure silver occur with copper-silver and gold-silver alloys [11]. A case of whisker-like crystal growth on gold jewellery in the Walters Art Gallery, Baltimore, has been mentioned by Weisser [12]. The crystals were of silver sulphide, illustrating the reactivity of silver within the gold-silver system under poor storage conditions, although the composition of the gold objects attacked was not reported. The rate at which tarnishing occurs in gold-silver alloys decreases as the gold content increases. Some experimental work by Tamman [13] was carried out using solutions of ammonium sulphide and sodium sulphide to determine the reaction limits in solution, that is, the limiting percentage of gold below which corrosion can be expected. For $(\text{NH}_4)_2\text{S}_2$ and gold-copper alloys a value of 51.5wt% gold was obtained, whilst for gold-silver alloys the value was 46.5%. Sodium sulphide solutions gave similar results. German [14] examined the sulphide tarnishing susceptibility of a number of low carat gold-silver-copper alloys in the cast condition. Evidence of tarnishing with the formation of Ag_2S in a dendritic pattern was found over a wide range of gold contents, from 41% to 81%. Indeed, Wise [15] notes that a gold content as high as 95% may be necessary to prevent tarnishing problems occurring in contaminated environments. This was confirmed in dental studies by Tuccillo and Nielsen [16] who found that 92% gold content was not enough to prevent tarnishing. Electron microprobe examination showed either silver sulphide or copper sulphide to be present in ternary gold-silver-copper alloys; in many cases the onset of tarnishing was associated with specific microstructural features. This was also

observed by the author during the exposure of polished sections of some gold-copper-silver alloys in a high concentration of hydrogen sulphide (2% v/v) at 80% relative humidity for 70 hours. Some of the sections were etched by the exposure to reveal grain boundaries and casting segregation as well as two-phase areas of precipitation in those compositions lying in the two-phase field of the phase diagram (see McDonald and Sistare [17], for further discussion of the ternary equilibrium diagram). The results of this test are briefly listed in Table 1, in which it can be seen that only an alloy with 80% gold content was unaffected. Figure 1 shows an example of an ancient Colombian tumbaga alloy with a heavily tarnished surface. Although the alloy contains about 20% gold, 70% copper and 3% silver, it has been finished by depletion gilding and has surfaces on both sides enriched in gold.

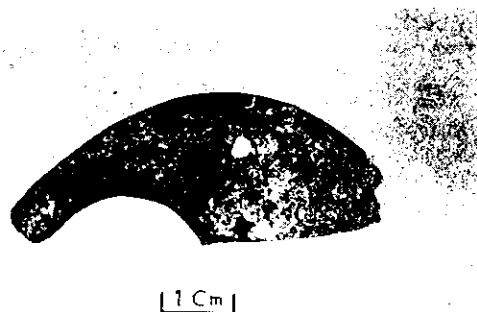


Figure 1 Fragment of a tumbaga alloy from the Nariño area, Colombia, from c. 10th–12th century AD, showing sulphide tarnishing.

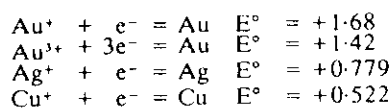
2.2 Dissolution of anodic constituents

Gold-copper, gold-silver and gold-copper-silver alloys as well as gilded surfaces are all liable to corrosion during burial. The process is usually aggravated by the presence of depletion gilded layers which are gold-rich compared with the underlying

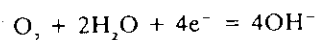
Table 1 Results of exposure of some gold alloys to H_2S at 80% RH for 70 hours. All compositions are in weight %.

Lab. No.	Condition	Au	Ag	Cu	Observations
A1	Worked	40	5	55	Moderately severe attack
A1	Cast	40	5	55	Severe attack
A2	Cast	57	25	18	Slightly attacked
A3	Cast	70	5	25	Slightly attacked
A4	Cast	58	12	30	Slightly attacked
A5	Cast	80	–	20	No attack
A8	Cast	49	11	40	Moderately severe attack
A8	Worked	49	11	40	Slightly attacked
A9	Worked	20	3	77	Severe attack

alloy. Part of the reason for the often severe corrosion which is observed is due to the large difference in electrochemical potential between gold, silver and copper:



Extensive work on the corrosion processes has been carried out by Tammann [18,19], Graf [20,21] and Forty [22] using a number of different gold-copper or gold-silver alloys. The results suggest that above about 50 atomic percent gold, corrosion will be very limited. This 50 atomic percent level corresponds to a composition of 75.6wt% gold, 24.4% copper, for binary gold-copper alloys, and to 64.6wt% gold, 35.4% silver, for binary gold-silver alloys. Figure 2 illustrates the sequence of attack in a gold-copper alloy during burial. If the surface is also depletion gilded, there will be an unfavourable combination of a large cathodic area and a small anodic area, at least initially. The usual cathode reaction under normal burial conditions is expected to be oxygen reduction rather than hydrogen liberation, and this is usually a four-electron process:



However, in corrosion couples with gold the evidence suggests that the reaction may be the two-electron reduction to peroxide:

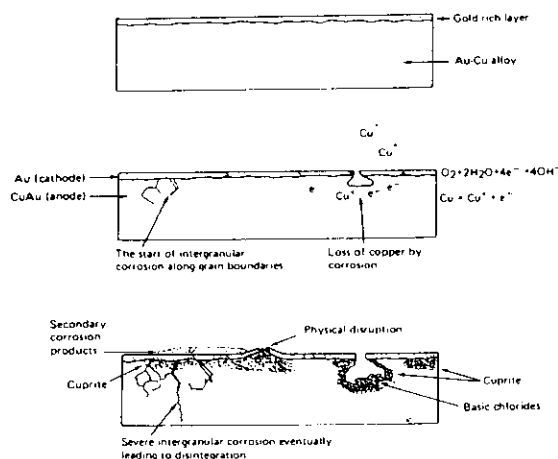
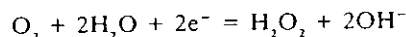


Figure 2 Example of corrosion processes in a depletion gilded gold-copper alloy. The sequence from 1 to 3 illustrates some of the features to be found in the corrosion. With low gold contents, the gilding may eventually detach itself from the heavily mineralized base alloy.

Detailed studies of the corrosion reactions in a variety of environments have been made (see Kühn [23]). In solutions containing chloride ions, such as may be present during burial, evidence for a corrosion-redeposition reaction has been found in which the gold ionizes as well as the copper and is then redeposited [24]. The following reaction is thought to occur, in which both Au (I) and Au (III) take part:

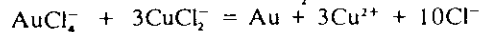
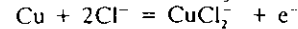
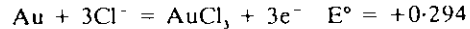
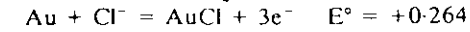
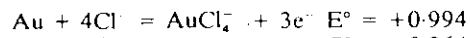


Figure 3 shows the polished sections of some gold-copper alloy fragments from Colombia. The objects were all depletion gilded and made in alloys whose compositions are given below:

Lab. no.	Area	Gold	Copper	Silver	Total
3	Tairona	36.6	39.7	3.6	79.9
96	Nariño	34.5	45.8	7.8	88.1
138	Nariño	22.2	64.8	2.2	89.2
149	Nariño	24.9	65.6	4.1	94.6

All the analyses were carried out by atomic absorption spectrophotometry and the incorporation of corroded metal in the sample taken is responsible for the low analytical totals. Examination of the microstructures shown in Figure 3 will make clear the reason for this: corrosion has deeply penetrated all of the fragments which have not only suffered extensive conversion to cuprite, but are also filled with cracks and voids where massive loss of copper has occurred. The presence throughout the alloy of both gold and copper means that local anode/cathode areas can occur, not just between the grains and the grain boundaries, but within the grains themselves. The corrosion in alloys of this type, therefore, is considerably more severe than that observed in pure copper under the same conditions. Beneath the gilded surface of many tumbaga alloys is to be found a black powder which is all that remains of the alloy itself. This black powder consists essentially of a finely divided gold in cuprite mixture, sometimes containing silver chloride as well. X-ray diffraction data obtained by Juleff [25], for a tumbaga fragment from the Nariño area, Colombia, is given in Table 2. The corrosion products are of the same types as found on corroding bronze as far as the copper compounds are concerned. These gold-copper alloys can therefore be progressively attacked by the formation of the copper trihydroxychlorides in the same way as other copper alloys. There are some differences, however; for example, layering of the corrosion products is not usually observed and the waxy nantokite (CuCl)



Figure 3 All samples mounted in polyester resin for metallographic examination and photographed in bright field reflected illumination. (a) Unetched $\times 36$, showing a section through a Tairona ornament cast by the lost-wax process. The polished section shows a coarse dendritic structure with extensive conversion of the alloy to cuprite (grey areas in the photomicrograph). The remaining sound metal appears white. Lab. No. 3. (b) Unetched $\times 1040$, high magnification view of part of a Nariño gold alloy sheet similar to Figure 3d, showing grain boundary cracking and embrittlement. The grey areas on the photomicrograph are corrosion products of copper. Lab. No. 138. (c) Unetched $\times 160$, section through a depletion-gilded Nariño sheet, showing the gilded surfaces surviving intact on both sides of a heavily mineralized gold-copper alloy. Massive loss of copper has also occurred (black areas in the grey matrix). Lab. No. 96 (d) Etched $\times 66$ (etchant: $(\text{NH}_4)_2\text{S}_2\text{O}_8/\text{KCN}$). Depletion-gilded Nariño sheet fragment, showing sound

metallic grain structure (twinned grains from working and annealing to shape). The black areas within the sheet are corroded lamellae orientated along the direction of working. Lab. No. 149.

layer often seen in heavily corroded bronze is absent altogether in the gold alloys studied by the author. Cuprite is the usual product below the surface or underneath the depletion gilded layer, the carbonates or trihydroxychlorides occurring at the surface or overlying the gilding.

Table 2 X-ray diffraction data for a Nariño tumbaga alloy of the Piartal period. The fragment is a piece of sheet with depletion gilded surfaces and is from the Municipio of Pupiales, Department of Nariño (about 10th–12th century AD). The composition (in weight %) is: gold 32.08, silver 3.13, copper 64.74.

Line spacing (d in Å)	Intensity	Probable identity
5.43	25	Cu ₂ (OH) ₂ Cl
5.01	20	Cu ₂ (OH) ₂ Cl
4.21	8	
2.85	14	Cu ₂ (OH) ₂ Cl
2.77	15	Cu ₂ (OH) ₂ Cl
2.74	15	Cu ₂ (OH) ₂ Cl
2.73	14	Cu ₂ (OH) ₂ Cl
2.64	8	
2.535	10	
2.46	12	Cu ₂ O
2.34	35	Au/Ag
2.255	25	Cu ₂ (OH) ₂ Cl
2.11	100	Au
2.09	8	Cu
2.03	15	Au/Ag
1.96	6	
1.825	80	Au
1.715	6	Cu ₂ (OH) ₂ Cl
1.502	6	
1.431	6	Au/Ag
1.291	70	Au

Note. Both atacamite and paratacamite appear to be present. ASTM data for atacamite gives major lines at 5.49, 2.77, 2.27, and minor lines at 2.75, 2.84, 5.04, 1.83, 1.72. Data for paratacamite includes major lines at 5.44, 2.27, 2.78, and minor lines at 2.76, 2.74, 2.72, 2.89, 1.71.

2.3 Stress-corrosion cracking and embrittlement

Depending on the conditions of burial, usage or even subsequent conservation treatments, a wide range of alloys used in antiquity may be susceptible to the form of corrosion known as stress corrosion cracking. This is particularly the case for alloys of gold with copper or silver. Even apparently sound gold-copper alloys may be extremely weak mechanically and crack or break when badly handled. The presence of intergranular stress corrosion cracking in such objects may be evident without any corrosion products being visible either on the surface of the object or in the body of the object itself. Alloys of gold with both silver and copper are vulnerable to this type of corrosion. There are a considerable number of factors which may lead to the presence of

some internal stress in both ancient cast and worked gold alloys. Wise [26], for example, notes that burnishing operations can create enough internal stress to induce stress corrosion, and the degree of stress here must be small compared with that in cold-worked gold-copper alloys. Even in the absence of stress, it has been found that gold-copper alloys which are susceptible to stress corrosion cracking can also be embrittled by intercrystalline corrosion. This is quite important for it is not possible to determine exactly what degree of internal stress existed in an ancient gold alloy at the time of manufacture, although by metallographic examination the grain structure, intercrystalline or transcrystalline cracks, extent of deformation and phase relationships can be evaluated.

A great deal of work has been carried out on the stress corrosion of gold-copper and gold-silver alloys, notably by Graf [27], Pickering [28] and Forty [29]. The behaviour of the alloys has been studied in aqueous solutions of ammonia, 2% ferric chloride, aqua regia, nitric acid, mercury, 10% potassium cyanide, and a number of other reagents. Even with the addition of a few percent of gold or silver, the alloys become susceptible to stress corrosion cracking. On the other hand, small additions of silver or copper to gold were not found to give rise to stress corrosion [27]. With further additions of gold to copper the susceptibility to stress corrosion increases until a maximum is reached, which is dependent on the nature of the aqueous environment. In general, alloys with from 10 to 30 atomic % are highly vulnerable (corresponding to about 25wt.% gold – 60wt.% gold for gold-copper alloys). The severity of the stress corrosion cracking then decreases as the gold content rises and should cease altogether once the gold content exceeds 40 atomic %. This corresponds to about 70wt.% gold for gold-copper alloys. There is, therefore, a wide range of compositions over which ancient gold-copper or gold-silver alloys are liable to stress corrosion cracking.

In order to test the reaction of gold-copper alloys to aqueous ferric chloride solutions in the absence of any stress, Graf [21] examined the behaviour of annealed copper and copper with 10 atomic % gold (about 25wt.%) content. Following immersion in a 2% ferric chloride solution, the specimens were tensile tested. The pure copper samples showed only small decreases in tensile strength, and fractured in a ductile manner. The gold-copper alloy specimens, on the other hand, exhibited considerable loss of tensile strength the longer they were exposed to the solution. In addition, the fracture of the specimen in areas adjacent to the surface became increasingly intercrystalline as exposure times increased. The severe anodic dissolution to which ancient gold-

copper alloys are liable may, in addition, create the possibility of stress corrosion cracking. The microstructure shown in Figure 3 for object number 138, at $\times 1040$ magnification, for example, shows severe cracking of the alloy as well as general anodic dissolution. Figure 4, on the other hand, which shows a fragment of a quimbaya lime-flask, displays extensive cracking due to embrittlement without the presence of general anodic dissolution. Such cracks may be present in the alloy without necessarily being visible from a surface examination by eye; sometimes the embrittlement of the alloy becomes apparent when a sample is taken for analysis. Such was the case with a gold alloy chisel from Colombia [30], which developed transverse cracking when cut with an oil-cooled diamond wafering blade under the low load of 50 grammes.



Figure 4 Broken piece of a 'Quimbaya' style lime-flask made in a gold-copper-silver alloy and hollow-cast by the lost-wax process over a core (now removed) and finished by depletion gilding. These 'Quimbaya' pieces are from Colombia and may date from the period 500-900 AD. The type of branched surface cracking evident in the illustration is typical of the embrittlement observed in these alloys. Dimensions: approx. 60mm across the gold spheres, the fragment being 42mm in length.

2.4 Changes due to order-disorder transformations

The possible changes in structure which can occur in alloys such as gold-copper-silver alloys can be classified in the following way:

- a) ordering;
- b) age-hardening;
- c) spinodal decomposition.

The best known reactions are those which give rise to ordered phases. Some of these phases (such as AuCu) are very difficult to work and special measures are sometimes taken to prevent the formation of these superlattice constituents. Quenching in

water, for example, will suppress the ordering process, and it is interesting to note in this connection the working practice recommended by an early Spanish document from Tamalameque [31] in lowland Colombia, for the treatment of gold alloys whilst in the process of fabrication:

... and in this way, placing it (a bracelet) in the fire, taking it out and putting it in water and hammering it on an anvil with the stones described they worked until they had increased its size many times ... (Tamalameque 1555).

This quenching technique will make the hammering out of the gold alloy much easier if the composition is such that ordering may take place. If ordered phases are present, or if they form over long periods of time, then the structure of the alloy will display less ductility and will be harder than the random face centered cubic crystal structure. Many papers have been published concerning the formation of these ordered structures but, so far, studies concerned with ancient gold alloys have not concentrated on this aspect of their crystal structure [25]. The ordered phases are: CuAu(I), CuAu(II), Cu₃Au(I), Cu₃Au(II) and CuAu₃. Addition of silver to the gold-copper alloys narrows the compositional range over which ordering is expected [32], but some recent studies [33] have revealed a complex picture in the ternary gold-copper-silver system. The phases also form when diffusion takes place between heated gold films over copper substrates [34]. In this case both Cu₃Au and CuAu were found to form; the limited ductility of these phases will mean that the gold-rich surfaces are more liable to fracture. The phase CuAu reaches an ideal composition at about 75.6wt.% gold, whilst Cu₃Au occurs at about 50wt.% gold. Many tumbaga alloys have compositions which correspond to these gold contents. There is, therefore, a potential role which can be played by these ordered domains in the embrittlement and general corrosion of gold alloys.

The second type of structural change can also take place over long periods of time because it is controlled by diffusion within the solid. This is the age-hardening process. If the alloy at equilibrium is two-phase then different heat treatments can be used to suppress precipitation and then to allow aging to take place at specified temperature ranges [17]. When the precipitation is discontinuous at the grain boundaries the alloy can become embrittled. A wide range of gold-copper-silver alloys are two-phased, which means that the possibility of age-hardening is not confined to certain limited compositions, as appears to be the case with the ordering reactions.

The third type of structure, that of spinodal decomposition, has been observed by Yamauchi [33]. The modulated structure can also lead to

higher hardness values which could contribute to subsequent deterioration. The fine scale of the differences in composition may also lead to enhanced anodic dissolution if the alloy is penetrated by corrosive agents, such as saline solutions in burial. The precise effects of these types of structural change on the long-term corrosion of gold alloys has not been investigated, so it is difficult to say how serious they in fact are.

3 Aspects of conservation

The conservation of corroded gold-copper alloys presents a number of problems concerned both with the preservation of technological evidence and with the stability of the object itself.

Since these alloys were frequently used for decorative purposes, there may be remaining traces of paint, textile impressions, other associated organic materials, or inlays of minerals or semi-precious stones. In addition, the variety of different gilding techniques which were used in the Old and New Worlds means that it is not always possible to distinguish between them merely on the basis of visual observation. In the case of South American material especially, a metallographic examination is an almost essential requirement if a correct interpretation of the technological information is necessary. This can frequently be the case if a particular conservation treatment is to be applied to the object. If already conserved objects are submitted for technological examination it is essential that the conservation documents are available. This, of course, is a general problem, but one which is especially important in the present case.

Where associated material, such as textile impressions, remains within copper corrosion products, a decision will have to be taken whether to reveal the golden surface of the object or whether to preserve the evidence of associated material *in situ*. This often cannot be decided without consultation with the owner or with the curatorial staff, although in an archaeological context the aim should be to try to preserve as much information as possible, which usually means keeping evidence preserved in corrosion products.

Visual impressions as to the state of a particular object, even when examined under a binocular microscope, may be misleading. An example of such a case is shown in Figure 5. It appears to be a pendant composed of a clay and charcoal core covered with thin gold leaf which is now flaking from the surface. On one or two areas where the gold has been lost, a faint dendritic pattern can be seen on the core. Subsequent examination showed, in fact, that this pendant had been hollow-cast by the lost-wax process over a core which is still *in situ*. Having

established that, it still appears as if the gold alloy used to make the casting is quite thin, as flakes can be detached from the black core. However, it was mentioned previously that heavily corroded tumbaga alloys appear black and powdery in colour. The core materials used in the production of lost-wax castings are also frequently black in colour. There is, therefore, a problem here in deciding what is core material and what is underlying corroded metal.



Figure 5 Coclé style gold pendant from Panama, length 91mm. The pendant is of some interest as it is cast over a core still *in situ* and is made in an alloy of composition 58.2% gold, 35.1% copper, 4.3% silver, which has been finished by depletion gilding. It is now heavily corroded and much of the gold is obscured by copper corrosion products which have also penetrated into the core.

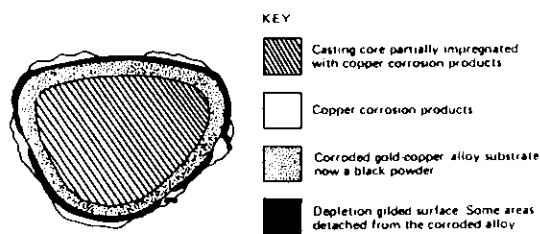


Figure 6 Sketch of a transverse section through the gold pendant shown in Figure 5.

Analysis shows, in fact, that the gold alloy has not been cast as a thin layer, but as a thicker gold-copper alloy, finished by depletion gilding. The boundary between the corroded alloy and the core material is visible in broken sections, but is nonetheless easily confused with the core itself. Copper corrosion products have been partially absorbed by the core and also disfigure much of the depletion-gilded surface. Some surface cleaning of pieces such as this can be attempted with non-ionic detergents in distilled water, applied carefully on swabs to remove encrusted dirt, whilst some of the copper corrosion products can be attacked with reagents such as dilute formic acid. Care must be taken to evaluate the dangers from chemical reagents seeping under the surface of such objects and being absorbed by the core. Gold alloy surfaces obscured by cuprite layers may be particularly difficult to deal with, since most reagents which can be safely used, such as formic acid, will only attack cuprite very slowly. Stronger complexing reagents such as ammonia or the di-sodium salt of EDTA may attack the copper below the surface too vigorously to be safe to use on corroded alloys of this kind.

There is a further difficulty with the cleaning of these gold alloys and that is the danger of flakes of the surface, or flakes of depletion gilding, becoming detached. This may be a problem for the conservator, whether he uses chemical cleaning, or careful mechanical cleaning with a scalpel under a binocular microscope, or even a combination of the two processes, which is frequently quite successful. There are essentially two problems here: one is to keep the alloy itself in a stable condition to prevent crumbling of the material, or loss of bits from edges or protrusions, and the other is to keep any gilded areas intact. In the first case a consolidant such as Paraloid B72 (an ethyl methacrylate copolymer) in acetone may be employed to impregnate the corroded alloy; vacuum impregnation is preferable. There are drawbacks to this process if the gold has been hollow-cast over a core which is still *in situ*, because the core may become consolidated as well, which might interfere with subsequent dating of charcoal-

rich cores, or otherwise invalidate future analytical investigations.

In the second case, where pieces of the surface may have become detached, they can be individually re-positioned with a suitable adhesive. It is sometimes possible to apply the adhesive in solution and allow capillary action to spread the adhesive under partially detached flakes. Careful surface cleaning can then be carried out without the risk of losing parts of the surface.

An awareness of the different types of deterioration to which gold alloys may be liable can be important background information to any proposed conservation treatment. Superficial tarnish, for example, is often removed from corroded silver objects using a mild abrasive, followed by careful degreasing and lacquering. This may work well on lightly corroded items but may not be so suitable for gold-copper or gold-silver alloys if they are rather fragile. In such cases a complexing reagent, such as a 5% solution of ammonium thiosulphate in distilled water, can be applied carefully with swabs. The thiosulphate will complex with silver sulphide to form argentothiosulphate complexes of the type $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$ and $[\text{Ag}(\text{S}_2\text{O}_3)_3]^{4-}$. In badly corroded alloys the cleaning solution may be absorbed into the object with the result that small pieces tend to become detached. It is safer in such cases not to attempt to remove superficial tarnish by chemical means. The method is quite successful on higher gold content alloys which are not permeable to aqueous solutions.

Another problem arises in attempted joins between broken pieces of tumbaga alloy. Since they often appear gold-rich and quite free of corrosion products it is easy to make the assumption that they can be joined together without difficulty. However, even using materials such as reversible cellulose-nitrate-based adhesives may result in a join stronger than the gold alloy itself; the pieces may then break along fresh surfaces with disastrous results. Failure of this kind can result from general corrosion or from grain boundary embrittlement, and such objects must be carefully supported both during conservation and in storage or display. Museum displays in which gold-copper alloys are suspended from hooks or wire should be avoided, both from the point of view of repaired objects and for the future stability of complete objects which can be badly strained by such treatment.

Very fragile pieces can be consolidated with a suitable resin, which will assist in retaining mineralized base metal, bearing in mind the potential problems associated with such treatments, such as the trapping of active corrosion and the difficulty of removal at a later date. As some of the gold-copper alloys suffer from the same corrosion processes as

occur in more usual copper alloys, such as bronze, it may be possible to effect some degree of stabilization by the use of a corrosion inhibitor, such as benzotriazole, followed by lacquering. Certainly some museum displays contain tumbaga alloys which appear to be undergoing progressive corrosion in the same way as other copper alloys. Research is required here to establish to what extent the stabilization of low-gold gold-copper alloys can be achieved by the use of benzotriazole.

Careful consideration must also be given to the storage and packing of fragile gold alloys. The use of polymethylmethacrylate sheets (Perspex, Plexiglas) should be considered as backing or mounting material for such items. Inert polyethylene foam packing materials are also very useful and can be cut to shape to house important or fragile objects, since many hammered gold alloy sheets cannot safely support their own weight. Moulded epoxy resin supports, such as those described by Eilertsen [35], may also be of some value if such objects have to be mounted for display purposes.

4 Conclusions

A number of problems remain in the conservation of corroded gold-copper alloys. The purpose of this discussion has been to cite some examples of deterioration and to examine possible corrosion processes. An awareness by the conservator and museum scientist of the fact that gold alloys can corrode is important, especially if collections containing substantial numbers of gold-copper alloys are to be cared for.

The technological information contained within these often severely corroded alloys should be preserved as far as possible and the conservator should be wary of applying chemical treatments in the removal of corrosion products, which might destroy part of the record of fabrication.

References

- GOWLAND, W., *The Metallurgy of the Non-Ferrous Metals*, 3rd ed., C. Griffin, London (1921).
- NEEDHAM, J., *Science and Civilization in China*, Vol. 5, Cambridge University Press (1974) 245-257.
- CRADDOCK, P. T., 'Gold in antique copper alloys', *Gold Bulletin* **15** (1982) 69-72.
- TYLECOTE, R. F., *A History of Metallurgy*, The Metals Society, London (1976) 37-38.
- CLARKE, R. R., 'The early iron age treasure from Snettisham, Norfolk', *Proceedings of the Prehistoric Society* **20** (1954) 27-86.
- LECHTMAN, H. N., 'The gilding of metals in pre-Columbian Peru' in *Application of Science in Examination of Works of Art*, ed. W. J. YOUNG, Museum of Fine Arts, Boston (1973) 38-52.
- DAS, H. A., and ZONDERHUIS, J., 'The analysis of electrum coins', *Archaeometry* **7** (1964) 90-97.
- SCOTT, D. A., 'Depletion gilding and surface treatment of gold alloys from the Nariño area of ancient Colombia', *Journal of the Historical Metallurgy Society* (in press).
- RAPSON, W. S., 'Effects of biological systems on gold', *Gold Bulletin* **15** (1982) 19-20.
- VERNON, W. H. J., 'Tarnishing of silver and silver alloys. Section IV of first experimental report to the atmospheric corrosion research committee', *Transactions of the Faraday Society* **19** (1923) 882-886.
- VINAL, G. W., and SCHRAMM, G. N., 'The tarnishing and detarnishing of silver', *Metal Industry* **22** (1924) pp.1, 15, 100, 151, 231.
- WEISSER, T., 'Structured questions section' in *Corrosion and Metal Artifacts*, ed. B. F. BROWN et al., NBS Special Publication 479, US National Bureau of Standards, Washington DC (1977) 228.
- TAMMANN, G., and BRAUNS, E., 'Das Verhalten von Gold und Legierungen mit Silber und Kupfer gegen Salpetersäure und Schwefelsäure', *Zeitschrift für anorganische und allgemeine Chemie* **200** (1931) 209-231.
- GERMAN, R. M., 'The role of microstructure in the tarnish of low gold alloys', *Metallurgy* **14** (1981) 253-266.
- WISE, E. M., 'Gold and gold alloys' in *The Corrosion Handbook*, ed. H. H. UHLIG, J. Wiley & Sons, New York (1948) 112-119.
- TUCCILLO, J. J., and NIELSEN, J. P., 'Observations of onset of sulphide tarnish on gold-based alloys', *Journal of Prosthetic Dentistry* **25** (1971) 629.
- MCDONALD, A., and SISTARE, G. H., 'The metallurgy of some carat gold jewellery alloys: part I - coloured gold alloys', *Gold Bulletin* **11** (1978) 66-73.
- TAMMANN, G., 'Die chemischen und galvanischen Eigenschaften von Mischkristallreihen und ihre Atomverteilung', *Zeitschrift für anorganische und allgemeine Chemie* **107** (1919) 1-240.
- TAMMANN, G., and WILSON, C., 'Die Änderung des galvanischen Potentials der Metalle usw', *Zeitschrift für anorganische Chemie* **173** (1928) 156-163.
- GRAF, L., and ATA, H. O. K., 'Untersuchung der Spannungskorrosions-empfindlichkeit von Ein- und Vielkristallen aus Messing und Kupfer-Gold-Legierungen', *Zeitschrift für Metallkunde* **64** (1973) 366-371.
- GRAF, L., 'The causes and the mechanism of stress corrosion cracking of homogeneous non-supersaturated alloys as derived from experimental work with alloys containing noble metal components' in *The Theory of Stress Corrosion Cracking in Alloys - The Proceedings of a Research Evaluation Conference*, ed. J. C. SCULLY, NATO Scientific Affairs Division, Brussels (1971) 399-417.
- FORTY, A. J., 'Micromorphological studies of the corrosion of gold alloys', *Gold Bulletin* **14** (1981) 25-35.
- KÜHN, A. T., 'Anodic dissolution, oxygen reduction and corrosion of gold alloys', *Surface Technology*

- 31 (1981) 17-31.
- 24 TISSOT, P., LOTHY, H., and MONNIER, D., 'Comportement anodique d'alliages or-cuivre en solution aqueuse de NaCl', *Chimia* 27 (1973) 15-18.
- 25 JULEFF, J., 'X-ray diffraction studies of gold', BSc Dissertation, University of London, Institute of Archaeology, 1981 (unpublished).
- 26 WISE, E. M., (Ed.), *Gold: Recovery, Properties and Applications*, Van Nostrand, New Jersey (1964).
- 27 GRAF, L., and BUDKE, J., 'Zum Problem der Spannungskorrosion homogener Mischkristalle III: Abhängigkeit der Spannungskorrosionsempfindlichkeit von Kupfer-Gold und Silber-Gold Mischkristallen von Goldgehalt und Zusammenhang mit dem "Mischkristall-Effekt"', *Zeitschrift für Metallkunde* 46 (1955) 378-385.
- 28 PICKERING, H. W., and WAGNER, C., 'Electrolytic dissolution of binary alloys containing a noble metal' *Journal of the Electrochemical Society* 114 (1967) 698-706.
- 29 FORTY, A. J., and ROWLANDS, G., 'A possible model for corrosion pitting and tunnelling in noble-metal alloys', *Philosophical Magazine* 43 (1981) 171-188.
- 30 SCOTT, D. A., and SEELEY, N. J., 'The examination of a gold alloy chisel from ancient Colombia', *Journal of Archaeological Science* (in the press).
- 31 TAMALAMEQUE, *Averiguaciones en Tamalameque Sobre los Manyllas que Mando Hazer Juan de Azpeleta a los Yndios de su Encomienda de Anpíhuegos* (1555) Justicia, Legajo 610-612 folios 2520-25 (manuscript), Archivo General de Indias, Seville (translation in the archives of the Museo del Oro, Bogotá).
- 32 HULTGREN, R., and TARNAPOL, L., 'Effect of silver on the gold-copper superlattice Au-Cu', *Transactions of the American Institute of Mining and Metallurgical Engineers* 133 (1939) 228-237.
- 33 YAMAUCHI, H., YOSHIMATSU, A. R., FORDUHI, A., and DEFONTAINE, D., 'Phase relations in copper-silver-gold ternary alloys' in *Precious Metals, Proceedings of the Fourth International Precious Metals Institute Conference*, Pergamon Press, Toronto (1981) 214-249.
- 34 PINNELL, M. R., and BENNETT, J. E., 'On the formation of the ordered phases CuAu and Cu₃Au at a copper/gold planar interface', *Metallurgical Transactions A* 10A (1979) 741-747.
- 35 EILERTSEN, K., 'A mounting technique for fragile metal objects', *Studies in Conservation* 26 (1981) 77-79.
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- Résumé**—On décrit les différentes manières dont les alliages d'or peuvent subir des détériorations. Les principaux alliages examinés sont des alliages Au/Cu, Au/Ag et Au/Cu/Ag. Les exemples utilisés à illustrer les différents types de corrosion proviennent d'alliages d'or sud-américains de Colombie et du Panama. Certains des problèmes traités sont relatifs à la conservation des ors antiques, et soulignent les difficultés rencontrés dans ce domaine.
- Auszug**—Es werden die verschiedenen Arten beschrieben, auf die Goldlegierungen beschädigt werden können. Die besprochenen Hauptlegierungen sind Gold-Kupfer, Gold-Silber und Gold-Kupfer-Silber. Es werden Beispiele südamerikanischer Gold-legierungen aus Kolumbien und Panama benutzt, um die verschiedenen Arten von Korrosionsangriffen zu veranschaulichen. Es werden einige mit der Erhaltung von Goldlegierungs-Antiquitäten zusammenhängende Probleme sowie die Schwierigkeit der Bewahrung technologischen Beweismaterials erwähnt.