The Surface Enrichment of Carat Gold Alloys – Depletion Gilding*

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Introduction

The techniques of surface enrichment of jewellery and other artefacts made from alloys containing gold have been practised for well over 2000 years. The techniques are known as *Depletion Gilding* or *Mise en Couleur* and, in essence, the process involves the removal of base metals and silver from the surface layers to leave them considerably enriched in gold. This is obviously radically different from other gilding processes such as electroplating, electroless plating and the older techniques of water gilding and fire gilding where gold is applied from an external source onto a substrate, usually of base metal or silver.

Similar changes in surface composition to enhance the colour and finish of carat gold jewellery are achieved nowadays using processes such as Wet and Dry Colouring, bright acid dipping and pickling and chemical 'bombing' with cyanide/peroxide mixtures although these do not necessarily all involve surface enrichment of gold. The last named process is particularly hazardous because of dangers of spillage and toxicity and there are other disadvantages as will be seen later.

There appears to be very little recently published or readily available practical information for jewellery manufacturers on these processes although Rapson has reviewed some of the scientific reports on selective dissolution and corrosion of gold alloys in acid media (1). This paper is an attempt to disseminate some of the information so that manufacturers are encouraged to investigate the use of alternative processes to chemical bombing.

Historical background

It is pertinent to briefly review the historical and archaeological evidence for depletion gilding because the treatments described have a relevance to some of the more modern processes such as wet and dry colouring.

The fact that base metals and silver can be removed by chemical means from gold alloys is well known. For example, when gold is assayed by cupellation (fire assay), "parting " with nitric acid is used to remove silver leaving behind a residue of fine gold. Similarly, refining by "inquartation" is done by alloying gold scrap with copper such that the gold content is not greater than about 25%. It can then be treated with nitric acid to remove silver and the base metals to leave gold. Many early cultures in different parts of the world used chemical means for the surface enrichment of gold-containing alloys and even for gold refining before nitric acid was available. In Europe, for example, nitric acid has only been in use since the twelfth century

Mediterranean Cultures

Analysis of fifth and fourth century BC Greek "white gold" and *electrum* coins has shown the existence of a gold-enriched surface layer with concentrations of over 70% gold being found in places, as compared to about 35% for the bulk of the metal (2,3). A cementation process was described by Pliny in the first century AD for refining gold. In this process, impure gold is placed in a crucible in intimate contact with a mixture of salt and brick dust and then heated. Base metals and silver are gradually removed from the gold and absorbed into the brick dust leaving behind a residue of relatively pure gold which can be separated from the brick dust by washing.

Another source of information on ancient techniques is the *Leyden Papyrus X*, a metallurgical text written in the fourth century AD by a goldsmith, and which contains recipes for refining, testing, alloying and soldering of gold, for gilding silver and other metals, and for the preparation of base metal alloys. An English translation of the text was published in 1926 (4) and discussed more recently by Hunt (5). Of particular interest in the context of depletion gilding is Recipe No. 25:

"For treating gold or for thoroughly purifying it and rendering it brilliant: misy 4 parts; alum 4 parts; salt 4 parts. Pulverize with water (to make a paste) and having coated the gold with it place in an earthenware vessel put in a furnace and luted with clay (i.e. sealed with clay) and heat until above named substances have become molten; then withdraw it (the gold) and scour carefully."

According to Pliny, misy is either iron or copper pyrites or their oxidation products, i.e. the sulphates.

Pre-Columbian Goldsmiths

The pre-Columbian cultures of Central and South America were highly skilled at metal working, and archaeologists have drawn attention to the methods that were used to produce gold-enriched surfaces on items made from alloys containing a low proportion of gold. Gonzalo Fernandez de Oviedo (1535-1548) wrote (6):

"... they know very well how to gild the objects and items they make from copper and low grade gold. And they have such ability and excellence in this, and give such a high lustre to what they gild, that it looks like good gold of 23 carats or more... They do this with a certain herb, and it is such a secret that any goldsmith in Europe or in any other part of

Christendom, would soon become a rich man from this manner of gilding."

The depletion gilding techniques that were most likely to have been used by the pre-Columbian Indians have been investigated by Lechtman (7,8). The alloys used were generally of two types. One type was known as *tumbaga*, reddish, bronze-coloured copper-gold alloys produced with differing gold contents, and probably containing silver as an impurity. The other type were pale greenish-white ternary silver-gold-copper alloys containing a high proportion of silver. These were not dissimilar to the *electrum* of the Mediterranean world and appear to have been widely used in Peru.

The methods used by the pre-Columbian goldsmiths also fall into two groups. The first is *Mise en Couleur*, a name given in archaeological circles to processes for depletion gilding objects made from tumbaga, in which the alloy was rubbed with the juice of a plant and then heated so that it assumed a gold coloration due to the removal of copper from the surface layer. This process could be repeated many times to increase the thickness of the gold-enriched layer and improve its colour. It is believed that the plant was a species of *oxalis* and that the juice contained oxalic acid. It is possible that ammonium carbonate soaked in urine was also used. Lechtman has pointed out that although depletion gilding of tumbaga works well with these processes, they do not remove any silver that might be present in the alloy.

Gold alloys of the electrum type containing high silver were probably gilded using a cementation process or by using special aqueous pastes. In the cementation process, the object to be gilded was placed in a crucible and surrounded with a powdered mixture which invariably contained alum (potassium aluminium sulphate), common salt (sodium chloride) and brick dust. The crucible and its contents were heated and the mixture reacted with the surface of the alloy to form chlorides of silver, copper and other impurity metals. The molten

chlorides were then absorbed by the brick dust. Additional ingredients may have been ammonium chloride, potassium nitrate, copper and iron sulphates, vinegar and urine. After cooling, and subsequent washing to remove residues, the brilliance of the gold-enriched surface was improved by burnishing.

An alternative method was to immerse an object to be gilded in an aqueous paste or solution of alum, iron sulphate and salt at room temperature. After about ten days, it was taken out and washed in a strong salt solution to remove surface scale. The object was then heated to convert the spongy, gold-enriched surface to a smooth compact richly coloured surface. Both the cementation and the aqueous paste methods work equally well on alloys with a high silver content and with tumbaga.

Figure 1 shows discs which were made in Peru probably during the early Vicus period. The classical Vicus period was between 400 BC and 100 AD, although there was a later period which extended to about 700 AD. It is thought that these particular discs are from the earlier period because of the lack of surface decoration. The discs had lain buried for many centuries and traces of black corrosion products may be seen in the micrographs of cross sections of the discs, Figure 2. A thin, gold-rich layer is clearly visible, which is surrounded by corrosion products in places. Tiny flecks of gold can be seen within corrosion products, Figure 3. These particular discs were made from tumbaga having high copper and low gold contents.

Figure 2 - Cross-section of Vicus disc showing depletion gilded layer. x200

Figure 3 - Vicus disc showing gold flecks in corrosion products. x200

The Vicus culture was followed by the Mochicas who excelled in a variety of metalworking techniques, such as raising, forging, chasing and lost wax casting using mainly the high silver-containing alloys, similar to electrum. They in turn were followed by the Chimu (1000-1470 AD) who were highly skilled in depletion gilding objects made from tumbaga and electrum type sheet.

Jacobson and McKenzie (9) and Scott (10) put forward the argument that low gold alloys containing copper were first heated in air to produce a black copper oxide scale and then treated to selectively remove the copper and silver.

Figure 1 - Depletion gilded tumbaga discs from the Vicus Period, Peru

Depletion Gilding Experiments and Workshop Trials

In 1981, the author of this paper, together with Teresa del Solar, an archaeology graduate from Peru who was studying silversmithing and jewellery at the City of London Polytechnic, did some experiments and workshop trials on depletion gilding using cementation and aqueous paste treatments similar to those described earlier. The aim of this short research programme was to see whether the techniques could be successfully applied to 9 and 14 carat gold-silver alloys (11).

The alloys were prepared using fine gold and silver grain by melting, casting, forging and rolling to 1mm thick strip with intermediate and final anneals. The hardnesses of the annealed strips were HV40.5 and 42.5 for the 9 and 14 carat alloys, respectively. The 9 carat alloy was white, whereas the 14 carat alloy had a distinct pale greenish-yellow tinge.

Two different pastes were prepared by mixing the powdered chemical compounds together with sufficient distilled water to form a thick paste. These were:

Alum paste
Potassium Nitrate 10 g
Sodium Chloride 9 g
Potassium Aluminium Sulphate (Alum) 5g
Iron salt paste
Ferrous Sulphate 10 g
Sodium Chloride 5 g
Potassium Nitrate 5 g

In some experiments, the pastes were used alone with samples cut from the alloy strips whereas, in the cementation trials, the pastes were mixed in equal parts with brick dust. Three types of crucible were used, namely, glass, porcelain, and porous earthenware pots used for assaying. The glass crucibles were unsuitable as only thin depletion gilded layers of poor quality were obtained. Porcelain crucibles were satisfactory only when brick dust was present. The porous earthenware pots were necessary to absorb the molten reaction products containing silver from the surface layers in the absence of the absorbent brick dust.

It is only necessary to summarise the results from the many experiments. Using electrically heated ovens or muffle furnaces, temperatures in the range 100 to 600°C and treatment times ranging from 15 minutes to several hours were investigated. The following trends were observed.

• At temperatures in the range 100-150°C, enriched layers of up to 7 μm in thickness were obtained but these had a patchy grey surface discolouration and grey inclusions were found within the layer. It is thought that these were due to the formation of silver chloride which could not be removed and absorbed either by the porous crucible or by brick dust at these relatively low temperatures.

• Better results were obtained in the range 150-200°C with only a few greyish patches being visible on the surface. Figure 4 shows a microsection of a 9 carat sample after 7 hours at 165°C in the alum paste without brick dust but in an earthenware pot. The layer thickness is 10-12 μm.

• At temperatures in the range 400-600°C, there was depletion of silver in the grain boundaries adjacent to the surface layer, Figure 5.

• Although both the alum and iron salt pastes yielded depletion gilded layers, the latter tended to give blackened surfaces as well as grey patches and inclusions and superior results were obtained with the alum paste.

Another variation in technique proved equally successful. In this, samples were placed in the alum paste with brick dust in an earthenware pot and gently heated with a torch for 3 minutes such that the paste melted but did not dry out. Although temperatures were not measured, the paste had an appearance similar to that when furnace heating to 150-170°C. After washing, the treatment could be repeated, with intermediate washing, as many times as necessary to build up the thickness and obtain the desired surface.

Some of the sections were subjected to electron probe microanalysis (EPMA) to analyse the variation of gold and silver contents in from the surface. Figures 6 and 7 show the gold and silver distributions inwards from the surface and Figures
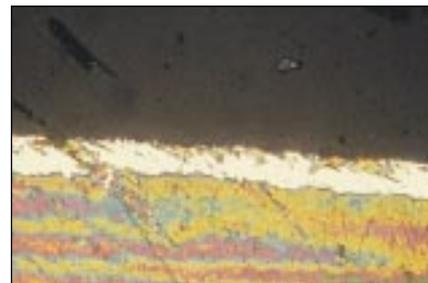

Figure 4 - 9ct gold-silver alloy treated 7 h at 165°C in alum paste. x250
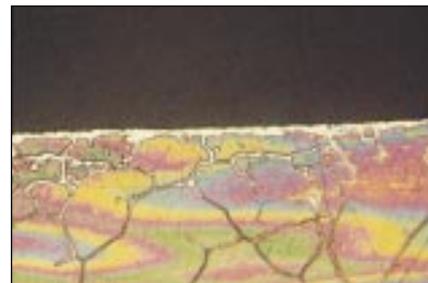

Figure 5 - 9ct gold-silver alloy treated 15 minutes at 600°C in alum paste. x250
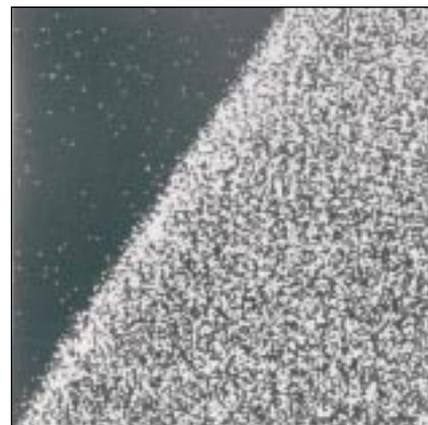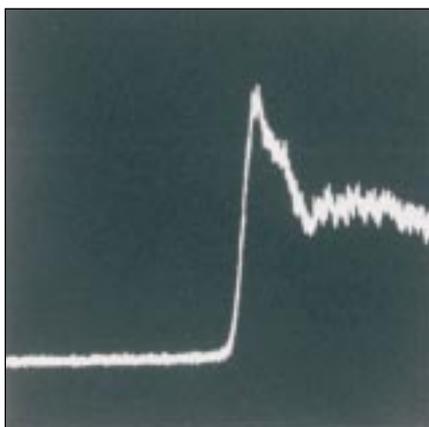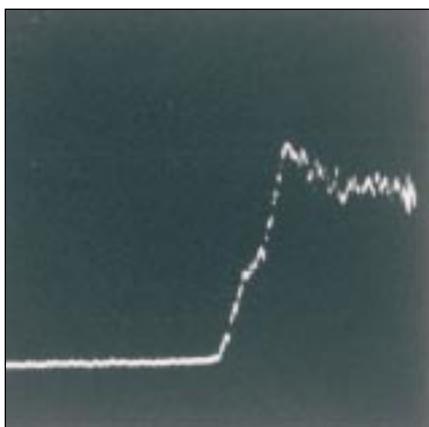

Figure 6 - EPMA analysis showing gold distribution inwards from the surface of 9ct gold-silver alloy given 9 cycles of torch heating in alum paste and brick dust.

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Figure 7 - As Figure 6 showing the silver distribution.

Figure 8 - EPMA analysis showing the x-ray intensity distribution of gold. Gold peak calculated to be 69%.


Figure 9 - As Figure 8 showing the x-ray intensity distribution for silver.

8 and 9 show the corresponding changes in concentration. The higher gold content at the surface can be clearly seen and was calculated to be 69% for this particular 9 carat gold-silver alloy sample, which had been given nine cycles of torch heating for 3 minutes followed by washing.

Because the gold-silver binary alloys were considered to be too soft for general jewellery applications, experiments were done also on a ternary 9 carat gold alloy containing 57.5% silver and 5% copper prepared as before. The annealed strip, which was again whitish in colour, had a hardness of HV 70. The results with regard to the quality and thickness of the depletion gilded layers were similar to those achieved with the binary alloys.

Additional treatments, not tried with the binary alloys, gave interesting results. A sample of the ternary alloy was heated for 14 hours at 450°C in a mixture of alum paste and brick dust in an earthenware pot. The surface layer produced was found to have an intriguing structure, Figure 10. The depleted layer was about 75 μm thick but contained islands of relatively undepleted material which EPMA indicated contained more copper than did the bulk of the sample. This might suggest that the silver is removed at a faster rate than the copper. The average gold content for this depleted layer was 51%. Similar structures have been observed in studies on the corrosion behaviour of gold-silver alloys in nitric acid, as will be discussed later.

One sample of the ternary alloy was heated in a boiling solution of alum (40g alum per 100 ml distilled water) for two hours. The resulting depletion gilded layer had a thickness of about 2 μm but was compact and had a good gold colour, Figure 11. The torch heating and washing technique was equally successful with the ternary alloy. Figure 12 shows a sample given nine cycles of 3 minutes in the alum paste/brick dust mixture with intermediate and final washings. The coating is 8-10 μm and of good quality. The advantage of these two techniques is that they are relatively easy to use in a workshop situation and the time to produce a layer of, say, 10 μm thickness is much shorter than with a single treatment in a furnace.
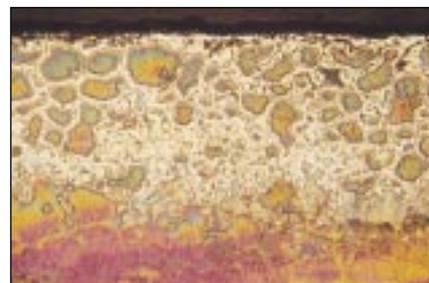
Figure 10 - 9ct gold-silver-copper alloy heated 14 h at 450°C in alum paste and brick dust. x200
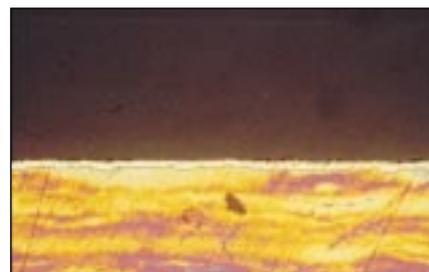
Figure 11 - 9ct gold-silver-copper alloy heated 2h in a boiling solution of alum. x400
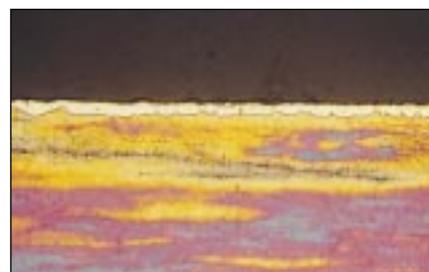
Figure 12 - 9ct gold-silver-copper alloy given 9 cycles of torch heating in alum paste and brick dust. x400

After the completion of the experimental work, Teresa del Solar demonstrated the possibilities for depletion gilding using the torch heating method on a series of plaques made from the ternary alloy with various designs on their surfaces. Areas where depletion gilding was not desired were covered with a resist and this was extended to give variations in the colour of the enriched surface by applying the resist at different stages of the heating /washing cycles. The reflectivity of the enriched layer was further enhanced by burnishing and also by finally heating in the presence of ammonium sulphide or sulphur to give what is often called an 'oxidised silver' finish to the undepleted regions. In fact, the characteristic brown-black surface colouration is due to the formation of sulphides. Examples of the plaques are shown in Figure 13 (a & b).

(a)

(b)

Figure 13a-b - Decorative plaques given varied cycles of torch heating in alum paste and brick dust.

Wet and Dry Colouring

There are old established chemical treatments, known as wet or dry colouring, which were widely used in the jewellery trade, if not today, for imparting a rich gold colour to the surface. These processes have been described in detail by Staton Abbey (12) and Ernest Smith (13). In essence, they are depletion gilding processes using the same types of treatments as described above. Two recommended mixtures* for wet colouring (13) are:-

	No. 1	No.2
Potassium Nitrate	100 g	100 g
Sodium chloride	50 g	50 g
Hydrochloric Acid	91.3 ml	91.3 ml
Water	45.7 ml	53.3 ml

* Converted to metric measures

It will be noted that the only difference is that Solution No. 2 is slightly more dilute. Nevertheless, Smith claims that this is better for 14 – 18 carat jewellery. He states also that alloys as low as 9 carat can be treated when suitable compositions are selected, preferably those with a low silver content. Some mixtures contain alum, e.g. potassium nitrate (100g), sodium chloride (50g) and alum (50g). Typical recommended procedures (12) are to gently heat, melt and boil the powdered compounds together with 40 ml water. Add 7 ml hydrochloric acid, reboil and then immerse the work to be coloured for, say, 4 minutes, remove and rinse in clean boiling water. Then 20 ml water is added to the colouring pot and then the immersion and rinse process repeated as necessary, with more water being added between each immersion.

Dry colouring is similar except that the acid and water are not added to the melt. Items are immersed directly in the melt when it boils up and starts to fume, held for a few seconds until the melt sinks down, withdrawn and pickled in hydrochloric acid pickle to remove the adhering mixture before repeating the process. Final burnishing further improves the rich brilliant gold colour. Both Smith and Staton Abbey state that dry colouring can only be used satisfactorily with 18 carat or higher quality golds. However, our experience would

suggest that considerable improvement in colour can be achieved in lower carat alloys using similar mixtures and it is possible that the important factors of process time and temperature, mixture composition and caratage and composition within caratage require a more thorough investigation.

Recently, it has been reported that a colouring solution containing a black sludge or powder is being used to improve the appearance of gold jewellery after immersion. It is said to give an 'Italian Colour' to the surface. It is known that the solution is based on sulphuric acid. Analysis of the solution and the black sludge by Inductively Coupled Plasma (ICP) Spectroscopy showed what chemical elements were present but not their compound form. Aluminium was found in both the solution and the sludge, where the level was particularly high. Although trace amounts were found of a number of elements, there were significant levels of lead, tin and cadmium. It is possible that these were impurities rather than deliberate additions. It is not possible, on the basis of these analytical results, to be sure what the colouring solution contains but there is a probability that aluminium is present as a sulphate in which case the solution is not too dissimilar from the solution described above for depletion gilding and wet and dry colouring.

A 'Rinse' powder containing a mixture of detergent and an unknown active agent was also being used by the same manufacturer. Analysis by X-ray fluorescence showed the presence of oxygen (72%), sulphur (15%), aluminium (5.9%), potassium (2%) and sodium (3%) together with silicon and phosphorus. This suggests aluminium sulphate or alum is the major constituent with phosphate and silicones typical of modern detergents.

Warning: Caution! Fumes arising from the boiling mixtures and solutions described above are injurious to health and adequate ventilation and use of a fume cupboard are essential. Again, care must be taken when adding water to these mixture but provided these precautions are taken, the processes are suitable for use in a workshop.

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Acid Pickling

Acid pickling has long been practised, primarily as a means for removing oxide films and flux residues after heat treatment and soldering operations.

A variety of pickling solutions, in terms of the acid strength, type of acid and bath temperature, have been used depending on the caratage and composition within caratage of the gold jewellery being treated. Smith (13) give a good account of common pickles and should be referred to if more information is required.

Importantly, acid pickles can selectively dissolve out the base metals and silver from the surface layers. Rapson and Groenewald (14) state that hydrochloric acid, sulphuric acid and *aqua regia* acid mixture have been used for colouring but that special procedures have to be followed if more than superficial surface enrichment is to be achieved. They state also that some gold is dissolved in addition to the other metals but is re-deposited onto the surface by electrochemical replacement methods. The technique works best with copper-rich alloys of 14 carat or lower.

These procedures have been outlined in one of a series of articles appearing in a trade journal published in Germany probably during the 1960's (15). Relatively strong acid solutions have to be used, otherwise only the copper is removed, leaving discoloured gold-silver surfaces. A solution of 1:1 sulphuric acid: water is recommended at 80°C. This dissolves some silver from the surface.

Warning: Caution! Always <u>add the acid to the water</u> in a thin stream with constant stirring. *Never add water to the acid* as heat is rapidly evolved, leading to boiling and violent ejection of acid, giving the risk of a serious accident to personnel.

For gold-silver-copper alloys, the following etchants are recommended (15). Water and chloride-free nitric acid mixed in the proportions 1:1 or 2:1. Both copper and silver dissolve in nitric acid but Reference 15 says that the copper dissolves earlier so that, after a short etching time, the colour appears too light. It is necessary to etch for a longer time to obtain the desired gold colour. It is also noted that if chlorides are present in the solution, silver chloride may be formed which is re-precipitated back onto the surface, causing discoloured patches.

It has been practice in many workshops (15) to gold 'boil' the higher caratage gold wares in pure hydrochloric acid to obtain a deep gold colour. Since the acid is non-oxidising, the silver or gold is not attacked and silver chloride is not re-deposited. However, there is a danger that with severely cold-worked, unannealed parts, the risk of stress corrosion cracking may be increased.

It should be noted that parts should not be held by clamps or wires of non-precious metal when immersed in acid pickles since these will be attacked and go into solution, causing re-deposition and unsightly coatings of the more noble metals.

A number of workers have studied selective dissolution from noble metal alloys. Notably, Forty and Durkin (16) and Forty and Rowlands (17) have studied the selective dissolution in gold-silver and gold-copper alloys in nitric acid and proposed a model by which the surface is enriched with gold. This work was reviewed by Forty (18) and discussed by Rapson at the 1995 Santa Fe Symposium (1). Briefly, the mechanism proposed is corrosion tunnelling, whereby the silver or copper atoms are removed, leaving gold atoms in the surface which form islands and grow by a reordering process involving surface diffusion, Figure 14. Alloys containing more than 50% gold rapidly form a continuous gold surface and passivate, i.e. the reaction is effectively stopped whereas with lower caratage alloys, the enriched surface will remain spongy and porous and continue to increase in thickness. It will be recognised that this is the principle of inquartation referred to earlier, whereby excess silver or copper has to be added to higher caratage gold alloys to obtain fine gold when boiling in nitric acid for assaying or refining.

Chemical 'Bombing'

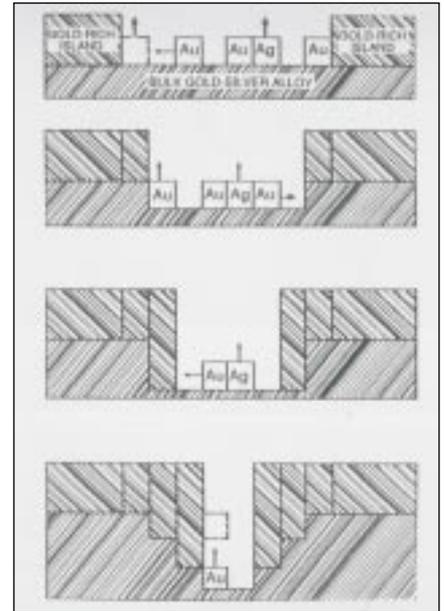In the early 1970's, a procedure for brightening gold alloys by chemical

Figure 14 - Corrosion and diffusion re-ordering model by selective dissolution. After Forty et al (15,16)

means was patented which has become widely known as *chemical 'bombing'* (19). Normandeau described the process in some detail at the 1990 Santa Fe Symposium (20). Essentially, jewellery wares are placed in a hot sodium or potassium cyanide solution at 80-85°C in a suitable reaction vessel. A roughly equal volume of 30-50% hydrogen peroxide (H_2O_2) is added and almost immediately there is a violent foaming and explosive reaction liberating oxygen gas. The reaction should be quenched with cold water just before it boils over. It can be appreciated that this is a hazardous operation and, at the very least, it should be performed in an efficient fume cupboard. The full <u>safety precautions taken when using cyanides</u> must be observed. Faccenda suggests that the process is gradually being abandoned and that relatively few companies are using it and then only with special 'closed circuit' equipment (21) to ensure safety.

Various concentrations of cyanide in solution have been reported ranging from 13 – 110 g/l but since cyanide is potentially very dangerous, the use of the lower concentrations is recommended (21). Indeed, Schneller has emphasized that there is no advantage in using higher concentrations and that the process can be more efficient at the lower concentrations (22). He has stated that 13 g/l is not only quite adequate but is safer. The reaction, in terms of weight loss, reaches a maximum at about 25 g/l and reduces at higher concentrations.

According to Normandeau and Faccenda, the base metals are dissolved in the cyanide leaving a thin surface layer enriched in gold. It may be necessary to repeat the process a number of times to achieve the desired result, particularly if lower concentrations of cyanide are used. Rapson and Groenewald say that the process can be used to restore the colour of white golds if they have developed a yellow tinge; presumably nickel-white golds due to phase separation.

Surprisingly, little seems to have been published on the mechanisms of dissolution in chemical bombing. One might expect that the base metals and silver and gold will all be selectively dissolved but that the rates of solution may vary with cyanide concentration. There is an extensive review of the reactions with cyanide in the book "The Metallurgy of Gold" by Rose and there it is stated that the rate of dissolution of gold goes through a maximum with increasing cyanide concentration and is reduced at high concentrations (23).

Normandeau has discussed also a further problem with chemical 'bombing' when using 10 carat cadmium-free solders which contain indium (20). Indium cyanide may be deposited as a discoloured corrosion product on the jewellery, requiring removal by additional finishing operations such as abrasive polishing. This, in turn, may produce a toxic dust and precautions would be required against inhalation. The corrosion problem was not observed with 14 and 18 carat solders containing indium.

Energy dispersive X-ray analysis showed that the chemically 'bombed' solder surface was depleted of gold and that the anticipated surface enrichment as a result of depletion of base metals was not found in the presence of the corrosion product. This might indicate that surface enrichment during 'bombing' occurs by re-deposition of gold onto the surface from the solution. Normandeau concludes that a simple solution to the problems of corrosion and the dangers of spillage and toxicity would be to eliminate chemical 'bombing' as a finishing process.

Concluding Remarks

The time has come, perhaps, to re-examine some of the colouring and surface enrichment processes in use in workshops earlier this century. At the time they suffered from a disadvantage that the surfaces obtained were matt or porous and it was necessary to burnish articles, usually by scratch brushing with soap lubricants. This may be acceptable for a few items but it hardly lends itself to modern mass production processing and was, perhaps, one reason why chemical 'bombing' appeared to be an attractive alternative. However, considerable advances have been made in recent years in mass finishing equipment and processing.

The use of pastes and absorbent materials such as brick dust are unlikely to be suitable for factory operations, although they may be for small workshops, but the use of solutions for immersion followed by rinsing and re-treatment, if necessary, should not present a problem. A final burnishing treatment using modern machinery may produce the desired finish in terms of gold enrichment and colour.

There are a number of variations when considering solutions. Boiling in a solution of 40 g/100 ml of potassium aluminium sulphate (alum) for two hours certainly produced an acceptable result with the 9 carat gold-silver and gold-silver-copper alloys and it is probable that some of the other solutions given earlier in the paper will give equally good results in perhaps a shorter time. Reference 15 quotes an earlier worker who recommends an etch of 100 g of potassium nitrate, 65 g sodium chloride, 60 g hydrochloric acid and 20 g water for thinner articles and one of 100 g potassium nitrate, 65 g sodium chloride and 80 g hydrochloric acid for general use. Filigree work will necessitate a further dilution, i.e. 50 g hydrochloric acid and 50 g water.

It may well be that some research and development work is needed to establish the best additives and concentrations for particular caratages and alloy compositions. The advances in analytical procedures will greatly assist in understanding the mechanisms of depletion and surface enrichment.

It is hoped that this paper will stimulate an interest in re-discovering techniques for surface enrichment and colouring, particularly if they can replace the hazardous operation of chemical 'bombing'.

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