Tarnish Resistance, Corrosion and Stress Corrosion Cracking of Gold Alloys

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Tarnishing, corrosion and stress corrosion cracking (SCC) of gold alloys are related phenomena. They present problems when they occur in gold jewellery, dental gold alloys and electronic devices. They are exploited, however, in the depletion gilding and finishing of gold jewellery; and in the extraction, refining and fire assaying of gold. There is still much that is not known about these phenomena, but a coherent picture of their mechanisms is emerging as a result of studies of not only gold alloys themselves, but also of other alloys. Aspects of this development are discussed.

Tammann's extensive studies (1) established that the resistance of gold to tarnish and corrosion is not greatly reduced by the addition to it of silver and base metals, so long as the gold content of the resulting alloy is not below 50 at.%. This corresponds to about 15.6 carat for Au-Ag alloys and to about 18 carat for Au-Cu alloys.

Tammann's observations are of limited significance, however, when considering the resistance to tarnish and corrosion in the three areas in which this property is of particular significance. These areas are firstly, the tarnishing, corrosion and stress corrosion cracking (SCC) of gold jewellery; secondly, the tarnishing and corrosion of dental gold alloys; and thirdly, the tarnishing of gold alloy contacts in electronic circuitry. The circumstances under which tarnishing and corrosion occur in these areas differ widely. They may occur under humid but not necessarily wet conditions in the case of gold jewellery and gold alloy contacts. The products of corrosion under such conditions tend to accumulate on the surface of the alloy as tarnish films.

In the case of dental alloys, however, only those corrosion products which do not go into solution in the saliva and which adhere to the alloy surface result in formation of tarnish films. Where the gold or gold alloy is applied as a coating, as in some decorative and many contact applications, substrate and other effects must also be taken into account.

Tammann's rule also suffers from the limitation that it takes no account of the variations in the microstructures of gold alloys which arise from the phase relationships which are applicable to them and

their metallurgical histories. Thus alloys which are homogeneous solid solutions and which do not undergo separation into two immiscible solid phases are in general more tarnish and corrosion resistant than those which are mixtures of two phases. In the latter case, as exemplified by some nickel white gold alloys, the one phase may contain too little gold to make it corrosion resistant. There is also the possibility of galvanic effects between the separated phases where the compositions of these differ significantly; and the formation of ordered Au-Cu phases may also lower corrosion resistance.

Grain size is a significant factor. Where it is very small the grain boundary energy can become a significant driving force for corrosion, supplementing the forces arising from electrochemical differences between the alloying elements and from galvanic coupling between segregated phases.

A further important factor in the case of some alloys is the presence of high internal stresses in the alloy created by working and which have not been removed by stress-relieving annealing or in age hardening. These can make some alloys susceptible to stress corrosion cracking. The fabricator of gold alloy products can therefore contribute significantly to making his products more tarnish and corrosion resistant. In the case of lower caratage products, however, he cannot do so completely.

Published information in this field is extensive in respect of both dental gold alloys and the gold alloys used in electrical contacts. In respect of carat gold jewellery, however, it is still very scanty indeed and is embodied in a limited number of publications (e.g.

2–14). Some of these relate to Au-Ag-Cu or Au-Ag-Cu-based dental alloys, but have direct relevance to the tarnishing and corrosion of gold jewellery alloys.

The deliberate superficial corrosion of gold alloys in electropolishing, in the mass finishing of gold jewellery and as a first step in the depletion gilding or surface enrichment of lower caratage alloys, as well as the smudge phenomenon and the interactions which occur between the skin and gold jewellery are not considered here.

TARNISH RESISTANCE

Assessment of tarnishing and rates of tarnishing

Until relatively recently assessment was done subjectively and therefore only qualitatively. It can be assessed quantitatively, however, as a colour change by spectrophotometry in terms of the colour coordinates of test specimens before, during and after tarnishing (4, 8,14). The use of this technique promises to revolutionize studies in this field, since it permits assessments of tarnishing rates.

Assessment of resistance to tarnishing

This involves the question of the environment for testing. This has proved difficult in the testing of dental gold alloys and of gold alloy contacts, and much of the available information in these fields relates to the development of test environments which simulate actual exposure conditions as closely as possible. So far, no generally acceptable procedures for testing gold jewellery have been developed and the difficulties involved make it unlikely that they will be established in the near future. Most investigators have therefore had to be content to employ the most widely used method for testing of dental gold alloys, namely the Tuccillo-Nielsen test (2–4). In this, specimens are exposed alternatively in a rotating container to a corrosive liquid and the saturated moist environment above it. The corrosive medium is normally an artificial saliva as used for testing of dental alloys, but in other cases more corrosive saline environments containing sulfites, or sulfides at various pH values may be used.

It has been found (5) in the case of a 14 carat alloy that under the conditions of the Tuccillo-Nielsen test, selective sulfidation of both Ag and Cu occurs.

Such 'environmental' testing may be supplemented by electrochemical observations in which potentiodynamic scanning is used to measure the current density at an electrode of the test alloy in a test

solution as it changes with both increasing (forward) and decreasing (reverse) potentials. From such data, corrosion currents may be calculated which reflect, with some qualifications, the resistance of the test alloy to corrosion.

Through the application of these two test procedures, Fioravanti and German (4) were able to conclude that the desirable microstructural features for resistance to tarnish and corrosion in low (ca. 50%) gold content dental alloys are large grains, a minimum of phase separation and an absence of precipitated and ordered phases.

No comparable data on low caratage jewellery gold alloys have been found. Since many 14, 10, and 9 carat gold alloys contain significant percentages of zinc, it is uncertain whether these conclusions are applicable to them also.

CORROSION

Background

Corrosion of carat gold jewellery can occur as a result of immersion in sea water, chlorinated water or other corrosive media. It normally involves selective attack on the less noble alloy constituents which is a feature not only of the tarnishing of carat gold alloys but also of their surface enrichment or depletion gilding. It is also accepted as an initiating step in stress corrosion cracking of gold alloys, and is of major importance in determining the biocompatibility of dental gold alloys.

Our understanding of the mechanisms of this type of corrosion is based largely upon studies of homogeneous Au-Cu and Au-Ag alloys. Some aspects of these studies will therefore be discussed.

Selective dissolution from homogeneous alloys

In the idealized situation as depicted in Figures 1 and 2 (11) selective dissolution of A atoms could be expected to occur preferentially from kink sites (K) in the surface steps where the atoms are least firmly bound. At sufficiently low potentials, the dissolution current should involve mainly less noble A atoms and should decrease as more and more kink sites become occupied by the more noble B atoms. Thereafter, dissolution can proceed only by removal of A atoms from non-kink sites (N) or from terrace sites (T), which requires a greater overpotential or activation energy. Finally, the alloy could be expected to become completely passivated when all the surface sites are occupied by the more noble B atoms only. This passivation stage should be reached after removal of A atoms from only a few

Figure 1 Schematic representation on an atomic scale of the surface of an alloy composed of dissolvable A atoms and noble B atoms (based on reference 11)
K is a kink site on a surface step
N is a non-kink site on a step
T is a terrace site

Figure 2 Schematic representation on an atomic scale of the formation of a pit in a low gold content Au-Ag alloy by dissolution of Ag atoms and inward migration of the vacancies formed (based on reference 11)

atomic layers at the alloy surface.

That this does not occur implies that mass transfer must accompany the corrosion reaction so as continuously to expose more of the less noble A atoms at the surface. This is currently perceived as occurring through the inward migration of lattice vacancies formed at the surface, which facilitates not only surface diffusion, but also volume diffusion of the less noble metal to the alloy surface.

It is well known, however, that although such passivation occurs with high (over 50%) gold content alloys, it does not occur with gold alloys of lesser gold content (1). This anomaly has been interpreted in terms of a corrosion-disordering/diffusion-reordering

model based largely upon electrochemical studies by Pickering *et al* (15–17), and upon micromorphological studies by Forty *et al* (18, 19).

In terms of this model, the lattice vacancies from the initial stage in the corrosion process migrate both on the alloy surface (Figure 1) and into the body of the alloy (Figure 2). This facilitates diffusion of gold atoms on the surface, where they form gold islands, and in the process expose more alloy to attack. It also promotes diffusion of alloy atoms from the body of the alloy to the surface, and in the process creates corrosion tunnels and pits. Both these processes can be observed in micromorphological studies.

In the case of low-gold alloys, the formation of tunnels and pits proceeds unhindered and leads to ultimate disintegration of the alloy. In the case of high-gold alloys, however, the higher gold content is seen as imposing restraints on the development of tunnels and pits. The precise nature of these restraints has not yet been fully established.

This corrosion-disordering/diffusion-reordering model nevertheless deepens our understanding of the well-known inquartation procedure which is used not only in the parting of the gold-silver bead in the determination of gold by fire assay, but also in the refining of gold alloys by treatment with acids. In this procedure, the gold content of the alloy is deliberately adjusted to below about 25% in order to facilitate the dissolution of non-gold metals, and the recovery of the residual gold in pure form.

Selective dissolution from heterogeneous alloys

The position in respect of the corrosion of heterogeneous (multiple phase) alloys is much more complex than that of homogeneous (single-phase) alloys discussed above. In the former more than one phase is exposed at the alloy surface, and these may differ significantly in composition and in susceptibility to corrosion. The state of affairs is well illustrated in the case of the nickel white gold alloys, in which the nickel-rich phase may contain little gold and may therefore corrode preferentially when the alloys are exposed to acid. To a lesser extent, this type of effect may also occur with some low caratage Au-Ag-Cu alloys. No reports of studies of Au-Ag-Cu-Zn alloys have been noted.

STRESS CORROSION CRACKING

Its nature and significance

Superficial tarnishing and corrosion are not the only forms of environmental attack to which gold alloys of

Table 1 *Dependence of the sensitivity to stress corrosion of homogeneous Au-Ag and Au-Cu alloys on their gold content when exposed to 2% aqueous FeCl₃ solution (24)*

	Gold wt. %	Gold at. %	Stress in kg/mm ²	Time to fracture of the specimen in minutes
(a) Au-Ag alloys				
	0	0	15	>10,000
	1.8	1.0	12	,500–3,000
	5.0	2.8	10	ca. 1,500
	10.0	5.75	11	ca. 300
	15.0	8.8	10	ca. 60
	33.3	21.5	10	ca. 1
	40.0	27.0	10	ca. 1
	50.0	35.4	10	ca. 60
	54.9	40.0	10	>3,000
	60	45.2	10	>10,000
(b) Au-Cu alloys				
	33.3	14	18	ca. 1
	45.1	21	18	ca. 1
	50.0	24.3	15	ca. 1
	55.0	28.3	18	ca. 1
	67.4	40.0	22	>10,000

low caratages of about 14 or less may be susceptible. Such alloys, depending on their compositions, their metallurgical histories and the environments to which they are exposed, also undergo stress corrosion (or season) cracking. This phenomenon, which is also observed in other alloys, involves the local rupture of the alloy under the combined effects of corrosion and stress at levels well below those at which failure might be expected to occur if these agencies were to operate independently. When it occurs there is little or no evidence of corrosion products or distortion of the alloy, and there may have been no external application of stress. Cases of this latter type are caused by internal stresses only. Stress corrosion cracking can develop very rapidly (Table 1) and in environments which cause no superficial attack on the alloy and might therefore be regarded as harmless.

Thus, SCC may be induced not only by exposure to acids during pickling but also a result of contact with reagents such as ink, traces of hydrochloric acid in the atmosphere, perspiration, etc. It has frequently been initiated at points of stress created in annealed low carat alloys by subsequent stamping. Articles such as fountain pen nibs, rings, chains, etc, provide well-known examples. Unless the stresses in such articles are relieved by annealing, they remain as focal points for attack by any reagent capable of inducing corrosion cracking. A case has been quoted (20) in which the collapse of hard rolled low caratage foil, stored as received from the supplier in its original packaging,

was found to be a result of attack by fumes of hydrochloric acid from an adjacent workshop. In the same environment annealed foil remained stable. Great care should therefore be taken to relieve stress in low caratage gold alloys wherever feasible.

Stress corrosion cracking of gold jewellery is not very common, because such jewellery is not often exposed to corrosive conditions. When it does occur, however, the root causes are usually twofold. First, inadequate relief of internal stresses resulting from working of the alloy during manufacture, and, secondly, exposure of the jewellery to corrosive conditions (e.g. in chlorinated water). It is not normally encountered, as mentioned above, in alloys of caratages above about 14. The subject has been reviewed in well referenced papers by Dugmore and Des Forges (21) and by Rapson and Groenwald (22).

Its mechanism

Two stages are generally accepted as being involved in stress corrosion cracking, namely crack initiation and crack propagation.

Crack initiation is seen as involving the formation and rupture of embrittling surface film on the alloy resulting from reaction between a base metal constituent of the alloy and the environment to which it is exposed. It is essentially an electrochemical step, and the sites at which it occurs depend on the localized distribution of stress and the adsorbed species. The sites have a high energy and occur at such places as the

intersection of the surface with grain boundaries and with dislocations or faults at the metal surface.

Crack propagation is more difficult to explain and its mechanism has been the subject of differing views for a number of years. One problem is that it may follow grain boundaries and result in intergranular stress corrosion cracking (ISCC) or occur across grains and result in transgranular stress corrosion cracking (TSCC). In both cases the initial stage is an electrochemical one, and there has been a natural tendency to try to explain the rapid propagation of the initial crack tip on a similar basis. Thus, the freshly exposed metal surfaces at the crack tip have been postulated to be highly reactive, with the result that electrochemical initiation and further cracking proceed continuously at rates which are vastly greater than those under normal equilibrium conditions. It has not been possible to demonstrate unequivocally whether, and if so to what extent, this actually occurs. An alternative explanation, for which increasing evidence has been coming available, is that cracking (brittle fracture) results from a rapid migration of lattice vacancies to the crack tip, where they weaken the structure and so promote further cracking.

This is the basis of a surface-mobility-SCC mechanism put forward by Galvele in 1987. In terms of this, environmentally induced crack propagation is due to the migration of vacancies along the crack surface under the influence of stress. The role of the environment is to change the surface self-diffusivity of the alloy. A recent study of SCC in a Ag – 20 Au at %

alloy (23), concluded that:

- (a) SCC mechanisms, such as anodic dissolution, hydrogen embrittlement or cleavage, could neither predict nor explain the recorded observations;
- (b) of the SCC mechanisms put forward so far, the surface mobility-SCC mechanism is the only one that explains from both a qualitative and quantitative point of view, the observations made in the investigation.

Finally, it should perhaps be noted that the studies of SCC in gold alloys have mostly been carried out on binary Au-Ag and Au-Cu alloys. No systematic studies of SCC in ternary and quaternary gold jewellery alloys have been noted.

Studies of homogeneous binary alloys

Most of the available information pertaining more specifically to the occurrence of stress corrosion cracking in Au-Ag, Au-Cu, Au-Cu-Ag and Au-Cu-Ni alloys has emerged from the work of Graf and his co-workers (24–26). Their work was done at a time when the only mechanism for crack propagation appeared to be anodic attack at the crack tip, for which cathodic areas were necessary at other sites.

Au-Ag alloys are fully solid solution in type, even at low temperatures, and the same applies to Au-Cu alloys which have been heat treated at 700–800°C and quenched in order to prevent phase transformations at lower temperatures. Table 1 shows the manner in which the sensitivity of such alloys to stress corrosion

Table 2 *The action of different reagents on a 33.3 Au–66.7 Ag alloy under a tensile load of 10 kg/mm² (24)*

Reagent	Concentration	Electrochemical action* current in mA	Time to fracture of the specimen in minutes**
HNO ₃	conc	0.8–1.0	
HCl+HNO ₃	3:1	2.5	
	(conc)		
K ₂ Cr ₂ O ₇ +H ₂ SO ₄	conc	2–3	60
KMnO ₄ +H ₂ SO ₄	–	2–3	
CrO ₃	2% aq	0.3	13
HCl	conc	0.2	40
H ₂ SO ₄	conc	0	>15,000
FeCl ₃	2% aq	0.8	3
CuCl ₂	2% aq	0.5	5
ZnCl ₂	2% aq	0	>15,000
CrCl ₃	2% aq	0	>15,000
NaCl	5% aq	0	>15,000
CuSO ₄	5% aq	0	>15,000
Fe ₂ (SO ₄) ₃	2% aq	0.1	160

*In a gold-silver cell

**For a 33.3 Au–66.7 Ag alloy under a tensile load of 10 kg/mm²

cracking was found by Graf (24) to vary with their gold content. In the Au-Ag alloys the sensitivity to stress corrosion, which is nil with pure silver, increases progressively with gold content to a maximum and then falls again to zero at a gold content of about 45 weight per cent. The Au-Cu alloys, studied over a narrower range of composition, show a similar trend. Clearly, at a certain level of gold content, the alloy is protected from stress corrosion, just as it is from superficial corrosion.

Au-Ag (and Au-Cu) alloys do not exhibit stress corrosion in all environments, however, and Table 2 indicates why this may be so.

It will be noted that only where the reagent is such that a current actually flows between electrodes of Au and Ag placed in it, does corrosion cracking occur. Graf concluded therefore that only those reagents capable of promoting dissolution of silver in an Au/Ag cell containing the reagent are capable of producing stress corrosion cracking in Au-Ag alloys. In other words only those reagents produce stress corrosion cracking, which can by dissolution of the less noble metal in the alloy, change the surface structure of the alloy.

In the case of exposure of Au-Ag and Au-Cu alloys to reagents which dissolve gold, such as aqua regia and potassium cyanide solutions, Graf and Budke (25) found that with aqua regia susceptibility to stress corrosion cracking reached a maximum between 20 and 35 atomic % Au as it does with other reagents. Up to 40 atomic % Au, attack on these alloys clearly occurred both by superficial and stress corrosion mechanisms, whereas from 40–100% Au stress corrosion is not operative and failure is by superficial corrosion only. With potassium cyanide solutions, however, Au-Ag alloys exhibited no susceptibility to stress corrosion cracking. This was attributed (25) to the fact that aerated cyanide solutions dissolve gold to form the very stable $\text{Au}(\text{CN})_2^-$ complex, so that any gold cathodic areas created by initial attack on active sites tend to be dissolved irreversibly. With aqua regia as the corroding agent, however, it was concluded that gold dissolved at the corroding surface is reprecipitated on the walls of cracks or crevices by the action of exposed solute metal, so that the cathodic areas then deemed necessary for stress corrosion cracking were created.

Graf (26) also concluded that in alloy solid solutions the reactivity of the grain boundaries and of disturbed areas on the grain surfaces is enhanced, and increases with the concentration of the solute metal up to a maximum of 50%. Thus, they observed that Au-Cu solid solutions which are susceptible to corrosion cracking under stress, also exhibit intercrystalline

corrosion even in the absence of stress. Perhaps of greatest significance, however, was the demonstration that this enhanced reactivity in the grain boundary areas of homogeneous solid solutions was further increased whilst they were undergoing flow or deformation. In the light of this the special role of tensile stresses in stress corrosion cracking of homogeneous alloys could be understood. Such stresses produce highly activated flowing areas at the base of notches, so that intercrystalline or transcrystalline cracks developed rapidly. In polycrystalline material the cracks would be predominantly intergranular, whilst with single crystals the cracks would be transgranular.

Studies of ternary and quaternary gold alloys and the effects of structural heterogeneity

In comparison with the susceptibility to stress corrosion cracking of homogeneous gold alloys, that of Au-Ag-Cu, Au-Ag-Cu-Zn and Au-Cu-Ni-Zn alloys is more complex.

In the case of Au-Ag-Cu jewellery, the position is that at low caratages and approximately equal percentages of silver and copper, the alloys contain two solid phases, one silver-rich Au-Ag and the other copper-rich Au-Cu. Both of these would be expected to undergo stress corrosion in 2% FeCl_3 solution. Nevertheless, Graf has stated that alloys containing these phases are not susceptible to such corrosion, even though homogeneous Au-Ag-Cu alloys may be attacked. The less noble phase was seen as protecting the more noble one, so that an incipient crack was blocked off as soon as it encountered the more noble phase.

In early production of 14 carat fountain pen nibs, for example, Loebich (27) has stated that when ternary Au-Ag-Cu alloys were used, it was found desirable to age the fabricated nibs. In the aged condition they did not undergo stress corrosion cracking in use, whereas if heated to the point where they became homogeneous, cracking by the action of the ink became likely. When certain 14 carat quaternary Au-Ag-Cu-Zn alloys are used, however, such ageing is apparently unnecessary. This could be due to the known limiting effect of the zinc on phase separation in these alloys. The susceptibility of alloys of this type to stress corrosion is apparently considerably influenced both by their zinc contents and by heat treatment. Analogous anomalies occur in the case of the white Au-Cu-Ni-Zn alloys and these have been discussed by Graf.

In the case of Au-Cu-Ni alloys, the two solid solution phases which separate from the homogeneous alloy on ageing are a nickel-rich phase containing a little gold and copper, and a copper-rich phase

containing high gold but little nickel. Graf points out that the latter phase might be expected to be susceptible to stress corrosion because the base metal (copper) is less noble than the other main component (gold). On the other hand, the former phase should show no tendency to stress corrosion because nickel and copper (as a result of passivation of the nickel) have about the same electrochemical potentials, and this expectation is confirmed in practice. Thus, aged Au-Cu-Ni alloys contain one phase which should be susceptible, and one phase which should not be susceptible to stress corrosion. The susceptible phase is, however, inhibited and in practice the non-susceptible nickel-rich phase is strongly attacked and leached out.

These examples illustrate the complex interplay of factors which determine the behaviour of multi-component gold alloys under stress in corroding environments.

Avoidance of stress corrosion cracking

Steps which can be taken to avoid corrosion cracking of low caratage alloys include the following:

- Ensure good housekeeping – i.e., do not store alloys in corrosive environments
- Do not pickle excessively
- Minimize residual stresses in the alloy. This has been discussed by Grimwade (9), who emphasizes the extent to which these stresses arise from non-homogeneous deformation during working (and stamping) and from differential expansion and contraction during heating and cooling due to temperature gradients within an article. Wrought or stamped articles for example can be given a stress relief anneal at 250°C for 30 minutes, followed by slow cooling. Under these conditions they retain the high strength and hardness built in by cold working but their internal stresses are reduced. Slightly different treatment is recommended for nickel white gold products.

If such steps as the above do not remedy the problem, it may be necessary to use a more noble alloy composition. This can be achieved not only by use of a higher caratage gold alloy, but also by incorporating a larger percentage of silver in the alloy (21) or by exploring the effects of additions of zinc.

Stress corrosion cracking problems have been discussed by Normandeau (28). Also, Heuberger, Pfund and Raub (29) have reported on the effects of various surface treatments and of galvanic coatings on the susceptibility to SCC of a low caratage Au-Ag-Cu-Zu alloy. They found that resistance to SCC was increased by plating the alloy with thick (pore-free)

coatings of pure gold. Surface enrichment of the alloy in gold by oxidation, etching and mechanical polishing gave better results, and a combination of this treatment with gold plating was especially effective.

Stress corrosion cracking of carat golds by mercury

Closely related to stress corrosion cracking in aqueous environments is the cracking of low carat golds and of clad or plated golds which occurs as a result of their exposure under stress to mercury.

Except that cracking results from preferential diffusion of the liquid metal at activated boundary sites, rather than from electrochemical attack and migration of lattice vacancies, stress corrosion cracking by mercury is very similar to stress corrosion cracking by conventional aqueous agents (30). Thus, SCC apparently does not occur with pure metals, and with homogeneous Au-Cu alloys, the susceptibility to corrosion cracking by mercury increases with copper content, up to a copper content of 50%, and then gradually decreases to zero again as the copper content is increased to 100%. Low melting solders in the liquid state can induce stress corrosion cracking in the same way as mercury.

Surface enrichment or depletion gilding of carat gold alloys

In this process, the surface of a low caratage gold alloy is enriched in gold by exposing it to media which preferentially dissolve its base metal components. As a result the surface layers are enriched in gold, and on polishing a product of more gold-like appearance is obtained. The use of acid media for this purpose has a very long history. Such media, usually in the form of acidic plant extracts, were used in Mycenae, Troy, Japan and South America. In more recent times, reagents such as hydrochloric acid, sulphuric acid (1:1) and aqua regia have been employed.

It was to be expected that the mechanism of this process would be similar to that discussed above for simple corrosion of binary Au-Ag and Au-Cu alloys. That this is the case has been demonstrated by Forty (31), who studied the effects of 50% nitric acid on thin single crystal films of Au₅₀-Ag₅₀ alloy, using transmission electron microscopy. He found that as the surface silver atoms were selectively dissolved, the residual gold atoms underwent surface diffusion to form a maze-like structure of gold islands. The islands grew and the channels between them shrank as corrosion proceeded, so that they finally formed thin epitaxial surface coatings of gold. Although these observations were made on single crystals of Au-Ag

alloy, it is probable that ternary Au-Ag-Cu alloys behave similarly, and that the role of burnishing in depletion gilding is to remove imperfections in the gold layer formed in the depletion step. The localized heat generated during burnishing would assist the process.

No analogous studies of the use of alkaline media such as the cyanide-hydrogen peroxide mixtures used in the finishing of mass produced jewellery items by the Mulnet (32) or 'chemical bombing' process have been noted.

organization, and has specialized in recent years in promotion of gold and its uses. He is the author of many publications, including a recent book (in press), entitled 'The Science and Technology of the Industrial Uses of Gold'. This paper is based partly on material in this book and partly on a paper presented at the 1995 Santa Fe Symposium on Jewelry Manufacturing Technology.

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Deposition of Gold and Silver Colloid Monolayers on Dendrimer-Modified Silicon Oxide Surfaces

The modification of glass, silicon and ITO glass surfaces with starburst dendrimers (see *Gold Bull.*, 1996, **29**, 16), has enabled research workers in Freiburg, Germany and Los Alamos National Laboratory, USA to deposit gold and silver colloid monolayers onto these surfaces. Georg Bar, Shai Rubin, Russell W. Cutts, Thomas N. Taylor and Thomas A. Zawodzinski (*Langmuir*, 1996, **12**, 1172) have described a preparative method which is very simple, requiring only two steps, i.e. immersing the substrate into the dendrimer solution and deposition of colloids. The resulting transparent films are stable for at least several weeks.

The structure of the resulting films has been investigated using X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and atomic force microscopy (AFM), and this has shown that the size distribution, particle separation, and degree of colloid monolayer formation can readily be controlled. The optical properties were examined using UV-visible spectroscopy and surface-enhanced Raman scattering (SERS).

Gold and silver colloids ranging from 15 to 80 nm in particle diameter have been deposited onto the dendrimer-modified surfaces. XPS data show that the dendrimers spontaneously adsorb

on to various silicon oxide surfaces - it is likely that some amine groups are protonated under the conditions of these experiments, thus imparting a net positive charge to the dendrimer layer. The driving force for adsorption of the dendrimers onto the surface then arises from the interaction between the positively charged protonated amino groups and the hydrophilic silicon oxide surface.

SEM and AFM showed that the noble metal colloid particles are well isolated and confined to a single layer, and that aggregation does not occur on the surface. Particle size, inter-particle spacing, and surface coverage can be controlled by varying the colloid concentration in solution and the immersion time of the substrates, resulting in tunable physical and chemical properties of the films. UV-visible spectroscopic data show that the microstructure directly controls the optical properties of the layer. The SERS studies are being used to elucidate the relationship between the nanoscale architecture and the optical properties of the films. This new technology could also have applications in control of particle size in the preparation of supported gold catalysts.

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