THE SCIENCE AND TECHNOLOGY OF GOLD

A Twenty-Year Perspective

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The past two decades have seen important advances in almost all areas of the science and technology of gold. After pointing out the increased availability of information on gold, the author of *Gold Usage* briefly reviews developments in some of the less well-known applications of gold, such as gold powders, amorphous gold alloys and colloidal gold.

Availability of Information on Gold

Even as late as the early 1970s scientific and technical information on gold and its applications was limited. Moreover, in the absence of computerized bibliographic data banks, its retrieval from the scientific, technical and patent literature was a most tedious task. In some areas, there was coverage in handbooks, treatises and texts, but these were limited in number [1-7] and for the greater part out of print. In addition, even in the most recent edition of the Gmelin Handbook, the volume dealing with gold [8] had been published as long ago as 1954.

This position has changed radically. Thus:

- The 20 volumes of *Gold Bulletin* now constitute a continuously expanding and updated encyclopedia on the science and technology of gold. The accessibility of their contents should be greatly increased by a 20-year index which is being prepared.
- A more recent book on gold and its uses is available [9], as well as a book on the chemistry of gold [10].
- *Aurum*, now in publication since 1980, presents *inter alia* scientific and technical data relating to gold alloys and their use in gold jewellery fabrication. The availability of data sheets setting out the significant properties of a wide range of gold jewellery alloys deserves special mention in this connection.
- Critical evaluations of the phase diagrams of some 93 binary alloys of gold have been carried out as part of the ASM International/National Bureau of Standards Data Program for Alloy Phase Diagrams. The work was carried out at the Carnegie Mellon University under the leadership of Professor T.B. Massalski and was funded jointly by the International Gold Corporation Limited and ASM International. The monograph [11] has more than 200 illustrations, 68 of which are phase diagrams. The text includes discussion of stable and metastable phases, order-disorder and magnetic transitions, thermodynamic calculations and modelling, discrepancies in data values, and controversial areas and uncertainties in diagrams. Tables list invariant reactions, crystal structures, lattice parameters and experimentally and thermodynamically derived parameters. The bibliography is complete up to the end of 1985.
- Publication is pending through The Institute of Metals, London, of a six-part monograph on ternary gold alloys by a team working under the leadership of A. Prince of General Electric Company Research Ltd. and with support from International Gold Corporation Ltd., Johnson Matthey and Co., G.E.C. Research Ltd. and Engelhard Industries Inc. Some 260 gold ternary alloy evaluations have been made.
- A bibliography on the constitution of multicomponent alloys has appeared [12].
- The world patent literature has been monitored by the International Gold Corporation Ltd. over the past few years and abstracts of those patents deemed of interest from the point of view of gold usage have been

published quarterly in *Gold Patent Digest* over the period 1983-1987 [12a].

- Consolidated Gold Fields PLC has continued to produce its annual surveys of the supply of and demand for gold. These surveys have been steadily refined over the years.
- On the initiative of Canadian gold producers a Gold Institute, based in the USA, has been established. The Institute highlights and promotes selected applications of gold and publishes a news-sheet under the title *Gold News*.
- An International Institute for Precious Metals has been established in the USA. This institute organizes, inter alia, annual conferences, the proceedings of which are published annually in book form under the title *Precious Metals*. These volumes contain reviews and research papers on different aspects of gold use.
- In addition to the above, a number of journals, conferences and symposia in the fields of medicine, dentistry, catalysis, electronics, metallurgy, jewellery technology, electroplating, etc. now attract review and research papers relating to gold.

As a result of the above, there is today no lack of published information relating to gold and its uses. The problem is rather that this information tends to be spread through a wide range of publications dealing with a variety of industrial technologies and covering many branches of science and technology.

Gold Chemistry

In stark contrast to the position in earlier years, the past two decades have seen remarkable advances in gold and organogold chemistry. The advances have been made possible largely as a result of the use of physical techniques for the determination of structures, and in particular the use of single crystal X-ray diffraction, multinuclear magnetic resonance and gold-197 Mössbauer spectroscopy. The rate of advance in this field is reflected in the compilations [13] of X-ray structural studies of gold compounds published in *Gold Bulletin* in 1984, 1985 and 1986.

Nevertheless, as of today only one of the very many compounds of gold which have been prepared and characterized can be regarded as an industrial product. This is potassium gold(I) cyanide, which is the form in which gold is used in most gold plating baths. Some more complex compounds do find important application in the treatment of rheumatoid arthritis [14], however, and still others are being studied as part of the continuing search for substances which can be used in the therapy of cancer.

Despite this limited use of gold in the form of its compounds there are, amongst the vast number of gold compounds which have now been prepared and characterized, many which have special properties such as solubility in organic solvents, volatility, superconductivity and structure which make them of potential interest in the production of surface coatings, catalysts, colloids etc.

Of special scientific interest has been the discovery and study of binuclear gold complexes, with closer-than-normal Au-Au distances, and of the cluster compounds of gold [15], the molecular structures of which consist of clusters of gold atoms, surrounded by ligands. Their metallic cores have been likened to embryonic metallic structures but it is unlikely that this is the case.

It is significant, however, that in gold, the relativistic effect [16] which involves most strongly the 6s electrons reaches a first and pronounced maximum. It results in strong s orbital contraction and a related expansion of the p and d orbitals, so that the energy levels of these electrons are closer to one another and the s electrons are very tightly bound. This effect explains many of the exceptional properties of gold such as its noble character, its colour, the high dissociation energy of the Au₂ molecule, and the short Au-Au distances in the metallic lattice. It also explains the high electron affinity of gold atoms and the formation of metallic aurides containing anionic gold [17].

From being a very dull element, gold has now become chemically a very exciting metal, which is attracting increasing attention from research scientists [18, 19, 20]. This augurs well for the development of new applications for its compounds.

Colloidal Gold

Recent developments in respect of colloidal gold have been reviewed by Turkevich [21] under the headings of historical and preparative aspects, morphology and structure, colour, coagulation, adhesion, alloying and catalytic properties. Although studied intensively, however, applications or potential applications for gold sols are still limited. The use of Purple of Cassius in the production of certain enamel frits continues. The electro-catalytic properties of gold sols are of interest to at least one company, and the behaviour of colloiddally dispersed gold in glass and polymers has attracted interest. In addition, it has been demonstrated that colloidal gold is effective, as is colloidal palladium, for promoting the autocatalytic plating of plastics [22] but so far as is known, it is not used for this purpose. The use of colloidal gold containing radioactive Au-198 for medical purposes continues.

Perhaps the most striking development in respect of colloidal gold, and the one which has made it perhaps the most familiar gold *chemical* in many laboratories, is its use as a cytochemical marker in electron microscopy [23]. Colloidal gold markers are essentially gold sols stabilized by the addition of one or other of a variety of macromolecules. The latter normally show no change in their specific bioactivity as a result of being bound to gold particles. When tissue sections are treated with such a marker, the gold particles tend to be fixed therefore at sites at which substances are present which react with the macromolecular *marking* material surrounding them. These sites can then be located by scanning or transmission electron microscopy. In this way, using suitable gold markers, antigens can be located on thin tissue sections.

An appreciation of how the use of this technique has expanded in an almost explosive manner can be obtained from a recent review of developments in regard to it [24]. Improved resolution using this type of technique has recently been reported [25]. Electron microscope visualization of single antigen-binding antibody fragments was achieved by covalently linking an undecagold cluster complex to a specific residue in each such fragment, so that the distance of the gold cluster from the antigen was a maximum of 5nm.

Use of a *silver enhancement* technique has been found to increase the detectability of small gold particles in immunogold labelling with small gold particles.

Gold Powders

Gold powders can now be produced by a variety of techniques, and in particular particle sizes and shapes can be controlled to a considerable degree [26]. In their production by chemical methods, the particle shape is determined largely by the conditions of precipitation, and especially by the type of reductant used, while the particle size is determined by control of the nucleation stage and the subsequent particle growth. Control over the formation of aggregates is achieved by the addition of colloidal materials during the precipitation to prevent adhesion of particles to one another.

Such controls are very necessary since the powders are used as components of soldering and brazing pastes, and of the thick-film gold pastes used especially in the electronics industry. Other areas of application which have called for similar controls have been the development of solid composites and of materials for the direct filling of teeth in dentistry.

Gold Composites

The period under review has seen considerable effort devoted to studies of the production and properties of both bulk gold composites and gold composite coatings. The objectives have been to develop materials with improved wear resistance or tribological properties, improved hardness, greater resistance to high temperature creep etc. These objectives have been achieved in most instances.

As dispersed phases, a wide variety of metallic oxides, carbides, nitrides, silicides, silicates, glasses and organic polymers have been studied. Attempts to generate oxides and nitrides from reactive metals dissolved in gold have failed because, apparently, of the slow diffusion of oxygen and nitrogen into gold. As a result bulk alloys have been produced by powder metallurgy techniques [9, 27-29]. Among the more interesting of recent developments have been those of gold-glass composites, which are suitable for the fabrication of such items as gold medallions [30], and of gold-cerium oxide composites, which show substantially improved performance in make-and-break electrical contacts [31].

The production of gold composite coatings has also been studied, using both electrolytic and electroless deposition techniques, as well as vacuum methods [9, 32]. As in the case of bulk gold composites, research has disclosed materials which are technically attractive for certain types of uses.

Surface Coatings of Gold and Gold Alloys

There has been an increasing flow of developments in regard to the use of gold and gold alloy surface coatings for decorative purposes, in electronics, in protection from radiant heat, and in other spheres.

Of the techniques used for their production, electrodeposition remains by far the most important and a future review will describe the exciting developments which have been and are occurring in this area. In comparison, electroless deposition is still little used. It is subject to the effects of many parameters, whose control is more complex than that of the many parameters which affect electrodeposition processes. Nevertheless, as a recent review [32] indicates, knowledge in this area is increasing both in respect of the mechanisms involved and the development of viable systems. The work of Sard and Okinaka and their colleagues [32] has been important in this connection. The recent development of an electrochemical method for determining the stability of electroless gold plating baths [33] should assist material-

ly in the development of viable plating systems of this type.

In regard to surface coatings formed by pyrolysis of liquid golds [34] and thick film pastes, there have been considerable advances in the technology of their use and in our understanding of the mechanisms of film formation, and of frit and reaction bonding to various substrates, especially in respect of thick film pastes [35]. This has resulted from the extensive application of the latter in the fabrication of microelectronic devices [9]. Perhaps the most exciting developments in this area, however, are in respect of the use of laser beams to effect the pyrolysis of thick film pastes. This has made potentially feasible the 'direct writing' of gold circuitry in microelectronics [36].

Despite the advances which have been made in the production and application of surface coatings of the above types, the most striking changes have been in respect of gold and gold alloy coatings applied by vacuum techniques. Not only are such techniques very suitable for use with gold, but the gold film coatings produced are of special importance in the fabrication of microelectronic devices and as heat reflective or conductive coatings on glass, high polymers and other substrates. Vapour deposition, sputtering and ion plating of gold and gold alloys have therefore been intensively studied [37, 38].

Morphology, adhesion and the growth and physical attributes of thin gold films formed by these methods on various substrates have come under intensive study. In regard to their physical attributes, diffusion between them and various substrates and films of other metals, electrical properties, electromigration, etc. have been especially significant technically and have been much investigated as an integral part of the development of the use of such thin film systems in microelectronic devices [39-44].

Chemical vapour deposition (CVD) is a relatively recent addition to the armoury of techniques for the formation of thin gold films. Where the films must conform to strict specifications as in the electronics industry, a problem with this technique is contamination of the gold with the non-gold products of the decomposition of the volatile gold compound used. That this problem can be overcome by the choice of appropriate volatile gold compounds has been demonstrated [45-47]. Moreover, it has been shown that photolytic decomposition by laser irradiation of at least one gold complex, namely trimethylgold-trimethylphosphine, can be used for the production of patterned gold films on indium phosphide substrates.

Focused ion beams have also recently been used to induce deposition of gold from dimethylgold hexafluoroacetyl-acetonate in the vapour phase. The potential of these and related observations has generated

renewed interest in the synthesis and study of volatile organogold compounds.

Metallic Gold and Gold Alloys

As indicated earlier, the phase diagrams of a very large number of binary and ternary gold alloys have been systematically evaluated. The basic information necessary for the formulation of gold alloys with properties suited for specific applications is therefore now more easily available for gold than it is for most other metals. Moreover, the dividends that can accrue from the use of such data are well illustrated by the recent development of a 990 gold-titanium alloy suitable especially for fabrication into jewellery [48].

Apart from this, there have been reviews of the alloys used in traditional carat gold jewellery production [49, 50] which give improved insight into their formulation and behaviour. Attempts have been made to improve both their compositions and the technology of using them. Thus basic studies [51] of the colours of Au-Ag-Cu alloys by ellipsometric methods have made our knowledge of the variations of colour with compositions of these alloys more precise and have stimulated interest in the objective measurement of the colours of jewellery alloys in terms of the C.I.E. (Committee Internationale de l'Eclairage) system. Effort has been devoted also to attempts to develop new 18 carat white gold alloys [52] and to improve other alloys in current use [53]. In connection with the latter the effects of minor additions of a variety of elements to gold alloys of different caratages have been studied [54, 55] as well as problems of grain growth and refinement [56].

Magnetic carat gold alloys have also been reported upon with special reference to their potential use in jewellery [57].

So far as the technology of using carat gold alloys is concerned, a number of studies have been reported of their investment casting [58-61], and there have been advances and important developments in machines for production of gold chains, and in soldering techniques.

The most significant changes have been in gold alloys used in dentistry. Up to 10-15 years ago, dental gold casting alloys, according to their type, contained about 62-96% of gold, and usually less than 10% of palladium plus platinum. Because their melting ranges are too low, many of these alloys are unsuitable for porcelain veneering. New alloys were therefore developed for porcelain veneering, which contained increased percentages of platinum group metals, especially palladium, and lower percentages of gold. Such alloys have now largely replaced the high gold dental alloys formerly in use.

The development of these new dental alloys, which must meet rigid specifications in regard to their capacity for bonding firmly to dental porcelain during the firing and especially the subsequent cooling of the veneered products has been the subject of much research and a number of reviews [62-64].

Bonding of Gold and Gold Alloys to other Metals and to Non-metallic Materials

The introduction of veneered dental gold alloy castings created a lively interest in the formulation of dental gold alloys with capacity for bonding strongly to dental porcelains, and the addition of small quantities of base metals to such alloys to promote such bonding is now general practice.

Similar additions of such bonding agents and of glass frit to gold pastes for application to alumina and other substrates in the microelectronics industry has also become common. Moreover in the bonding of thin gold and gold alloy films to glass and other substrates the application of undercoatings to promote bonding is generally practised [9, 65]. In the decoration of ceramic ware using liquid golds, loss of the gold film as a result of the action of detergents continues to be a problem. Its study from both the ceramic and the metallization viewpoints could be rewarding. In the application of thin gold films to plastics the importance of surface preparation of the plastic in some instances is recognized.

Just as technical requirements have stimulated developments such as these, so has the need to bond fine gold wire to gold-coated surfaces in many microelectronic devices stimulated extensive research into such bonding as promoted by heat, heat plus pressure, ultrasonic and other means [66]. The development of successful high-speed automated techniques for the purpose has resulted in the manufacture and use of specially prepared gold bonding wire on a very considerable scale [67-69]. Thus, the length of such wire produced annually in Japan is about 250 000 km.

When the wire is drawn energy is stored in the metal as a result of the formation of dislocations and lattice defects. This strain energy is released as the metal recrystallizes, and its magnitude depends on the extent to which the metal has been worked, and determines the temperature at which recrystallization occurs in the wire during storage or use. Since recrystallization leads to grain growth and loss of mechanical strength, research has been devoted to the discovery of elements which, when added in trace amounts to the pure gold before drawing, will not only restrict grain growth but also raise its recrystallization temperature. As

a result, minute quantities of dopants such as Al, Be, Ca, Pb, Ti and Sn are generally added to the 99.999% gold used for bonding-wire production. Apart from this strict control over grain growth and recrystallization temperature, bonding wire must meet exacting specifications in respect of its mechanical properties in order to make it suitable for use in the automated bonding machines employed in the microelectronics industry.

Amorphous Gold Alloys

Since the first alloy (an Au-20at.%Si) was produced in an amorphous state by Klement, Williams and Duwez in 1960, research on rapidly quenched gold alloys has developed rapidly in step with that on other metal systems [70].

Amorphous binary alloys of Au with Bi, Fe, Ge, Hg, Sb, Si, Sn, Te and Ti and with a number of rare earth elements have been reported upon. Several amorphous ternary gold alloys and one amorphous quaternary gold alloy are also known.

The amorphous binary alloys of Au with Si and Ge have been extensively studied. They are formed easily by quenching from the melt because of the deep eutectics which exist in their equilibrium phase diagrams. Such deep eutectics are well established as favouring the formation of amorphous alloys by quenching. These binary alloys have also been produced in an amorphous state by other methods such as sputtering, evaporation, laser-melt-quenching and ion mixing. The kinetics of formation of these alloys and their stability have been studied as well as their physical properties, especially their electrical characteristics and superconducting behaviour at low temperatures.

The Au-rare-earth binary alloys are also distinguished by deep eutectics and therefore also form glassy alloys easily on rapid quenching from the melt. Quenching rates of 10^6 - 10^7 K/s are sufficient for the purpose. They have attracted much academic interest because of anomalous changes in their electrical resistivity as their temperature is decreased.

Only two uses have been proposed for gold-based amorphous alloys so far. Au/20-40at.%Si and Au/20-40at.%Ge have been suggested [71] for use for watchcases, where their superior hardness, tensile strength and corrosion resistance are seen as advantageous. Amorphous Au₅₅Pb_{22.5}Sb_{22.5} alloy has been studied for use in inertial confinement fusion (ICF) target applications [72]. The technique involves focussing an intense energy source on the surface of a spherical pellet containing the deuterium-tritium fuel. This produces an implosion of the

fuel mixture inside the pellet, which raises the fuel to its ignition temperature. The Au-Sb-Pb alloy was suggested for this application because of its low melting point, and the high degree of sphericity, smoothness of surface and uniform wall thickness of fuel pellets made using it. Moreover, as a glass, it can be expected to deform homogeneously and isotropically in an ICF implosion. Spherules of the alloy have been produced by both gas atomization and a pendant drop method.

It is possible that amorphous alloys of Au with Si and Ge may find use - like certain other amorphous alloys - in soldering and brazing applications and the same may apply in respect of amorphous Au-Sn alloys close to the eutectic composition.

Miscellaneous

Within the limited scope of this article, it is not possible to do more than simply mention developments that have taken place in many other areas of gold usage technology. These include the use of gold in :

- Microelectronics, and especially in the production of connectors and contacts to semiconductors [73],
- Photographic flash devices,
- Photographic films [74, 75]
- Phosphors [76] for use, for example, on TV screens,
- The glazing of buildings [77],
- The form of radioisotopes in medicine [9, 78],
- Solar energy devices [79],
- Special soldering and brazing alloys [9],
- Catalysts [80] and,

A large number of high technology instruments for monitoring and controlling temperature, pressure, humidity etc. [9].

Such miscellaneous applications are steadily increasing in number.

Conclusion

In the last two decades our knowledge of gold and its uses and potential uses has expanded steadily, in step with that on other metals. As a result, its industrial applications are no longer confined to traditional areas such as jewellery fabrication, decoration and dentistry. The special attributes of gold have created lively demand for it in a large number of scientific and high-technology applications, and especially in microelectronics. These - and the need to use gold efficiently to avoid the use of cheaper metals in its place - have provided the incentives for an ever in-

creasing volume of research on gold. This state of affairs should continue, with the uses of gold becoming more diverse in a variety of high technology applications in the future.

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