Gold-Platinum Alloys

A CRITICAL REVIEW OF THEIR CONSTITUTION AND PROPERTIES

By A. S. Darling, Ph.D., A.M.I.Mech.E.

In the second part of this article, concluded from the April issue of 'Platinum Metals Review', the author deals with the mechanical and physical properties of the gold-platinum alloys, their melting and working technology, resistance to oxidation and corrosion, and finally with their applications in industry.

In spite of their corrosion resistance and high mechanical properties certain inherent characteristics of the gold-rich alloys diminish their industrial significance. Because the shape of the diagram tends to induce slight composition variations, the response to age-hardening of alloys containing approximately 70 per cent by weight of gold is somewhat erratic. Homogenisation and solution treatments cause considerable grain growth, and the ductility of some of the age-hardened alloys is rather lower than desirable. In an endeavour to minimise such defects, third element additions have been made to gold-platinum alloys for many years.

Iron was once commonly used for this purpose. Although 0.2 per cent by weight of iron ensures an effective age-hardening response from material containing up to 94 per cent of gold (41) it does not inhibit grain growth and has little effect upon the ductility of age-hardened material. Similar objections apply to rhenium and magnesium (45, 46), both of which expedite the hardening process. Rhodium and ruthenium are the best general purpose additions (40, 42, 43). Rhodium is the element now generally added to the alloys used for the manufacture of spinning jets. Provided that a suitable quantity is added considerable advantages accrue.

The basic effect is to broaden the miscibility gap (40), and it is also claimed that 0.5 per cent of rhodium is sufficient to displace the two-phase region up to the solidus, thus turning the system into one of the peritectic type (39). Some fairly recent metallography by Schmid (36) tends to support this hypothesis. Table II illustrates the effect of rhodium additions of 0.5 per cent upon the mechanical properties of three heat-treated gold-platinum alloys (40). The rhodium endows the 75 per cent gold alloy with

Table II

Effect of Rhodium Additions upon the Mechanical Properties of Three Heat Treated Gold-Platinum Alloys (Ref. 40)

Au–Pt	Vickers Hardness		U.T.S. Tons/sq. in.		Elongation per cent	
	No Rh	With Rh	No Rh	With Rh	No Rh	With Rh
75 – 25	100	220	27.3	52.7	16	21
70 – 30	208	258	44.3	62.2	13	18
60 – 40	300	310	79.5	76.0	10	14

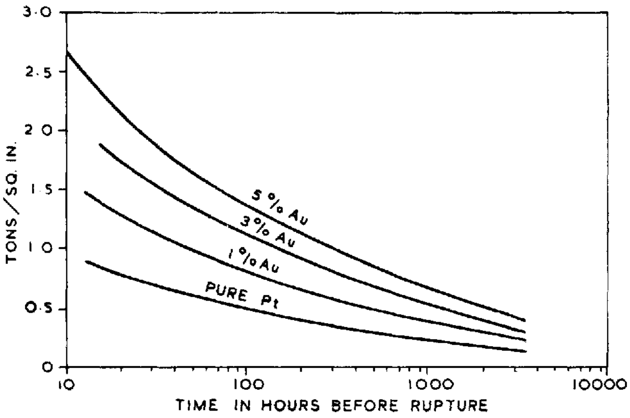

Fig. 12 Effect of gold additions upon the time to fracture of platinum at 900°C

considerable response to heat treatment. Rhodium contents greater than 1 per cent are less effective than smaller additions, the optimum quantity for the 75 per cent gold alloy, which does not normally age-harden, being about 0.5 per cent (42).

Because rhodium broadens the miscibility gap it facilitates the manufacture of hardenable spinning jets from the cheaper and more workable alloys. In some instances, however, operating conditions justify the employment of alloys containing approximately equal quantities of gold and platinum (39, 43). Such spinning jets are usually perforated in the soft condition, quenched, and finally aged. Rhodium additions reduce considerably the quenched hardness of alloys containing 35 to 80 per cent of platinum. Claims of improved ductility after ageing within this composition range are not fully substantiated when the platinum content exceeds 45 per cent (36).

Mechanical Properties at High Temperatures

Gold additions improve the creep resistance of platinum at moderately high temperatures. Fig. 12, which summarises the results of some time-to-rupture tests made at 900°C (37), shows that 5 per cent of gold increases the tensile strength of platinum for a given life by a factor of three. The presence of gold increases a tendency towards intercrystalline separation under stress; rhodium-platinum alloys, being less prone to this defect, are more generally suitable for high temperature service. Gold-platinum alloys are, however, more resistant to wetting by molten glass. This characteristic can be profitably utilised in some high temperature applications.

Electrical Properties

Alloys quenched from the single-phase region have well defined resistivities, as shown by the outer curve of Fig. 13, which indicates that 50 per cent of gold raises the resistivity to a rather flat maximum of approximately 44 microhm-cm. The electrical properties of alloys quenched from the duplex region depend upon the temperature of heat treatment and the extent to which equilibrium has been attained. Fig. 13, based upon the data of Johansson and Linde (10), indicates the resistivity at room temperature of alloys which, after slow cooling over a period of 72 hours from 1000°C, were quenched after 156 hours at 500°C or 39 hours at 800°C. Since the structure is a mechanical mixture of two solid solutions the resistivities of all

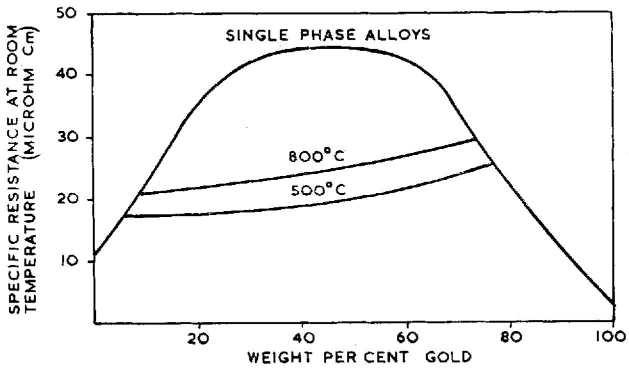

Fig. 13 Electrical resistivity of single phase and duplex gold-platinum alloys

duplex alloys vary with composition in an approximately linear manner. The time taken to approach a constant resistance value depends upon composition, and within regions of retarded precipitation can be very lengthy. This characteristic is well illustrated by the results of Johansson and Hagsten (29).

Fig. 14, largely based upon the results of Geibel (44), Johansson and Linde (10), and Wictorin (13), illustrates the mean instantaneous temperature coefficients, over the temperature ranges indicated, of alloys quenched from the single phase region. Most of these alloys are in a metastable condition and the values indicated apply only as long as the single phase structure is retained.

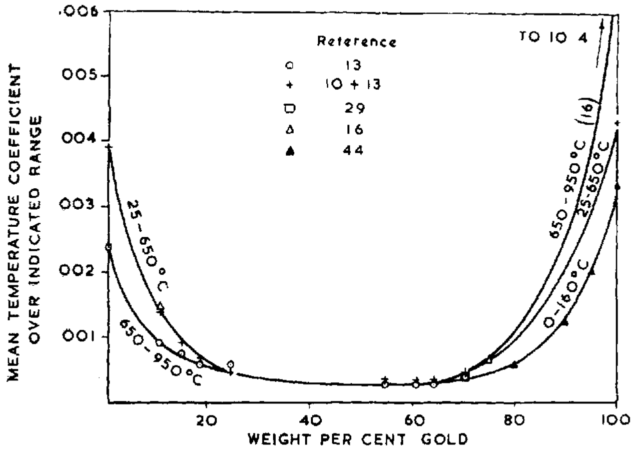

Fig. 14 Mean instantaneous temperature coefficients of gold-platinum alloys quenched from the single phase region

Careful studies of the resistance variations of specimens brought into some semblance of equilibrium within the duplex region have been made by Wictorin (13) Grube, Schneider and Esch (16), and Johansson and Hagsten (29). The compositions of the two phases change rapidly at temperatures above 700°C, and the apparent temperature coefficients, which increase at a rate largely determined by the slope of the limiting solubility curve, are many times higher than those of the single phase alloys.

Information on the instantaneous temperature coefficient at room temperature of alloys quenched from the duplex region has not been published, but it is reasonable to expect, as in the case of resistivity, a linear dependence upon composition between the limiting values of the terminal solid solutions. All the alloys have a negative thermal e.m.f. with respect to pure gold. Fig. 15, from Johansson and Linde (10), illustrates that the maximum e.m.f., of 19.5 microvolts per °C at 18°C, is generated by the 65 per cent gold alloy.

Physical Properties

The density composition curve shown on Fig. 16 displays a slight positive deviation from linearity in accordance with the corresponding negative deflexion on the lattice

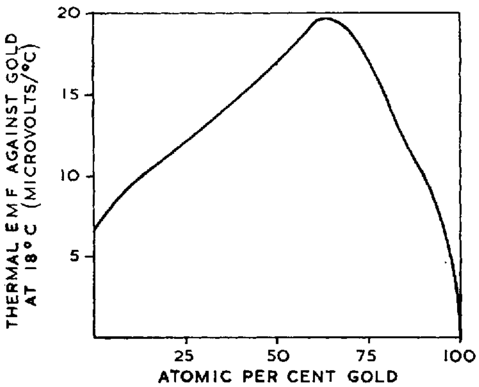

Fig. 15 Thermal e.m.f. with respect to pure gold or gold-platinum alloys (10)

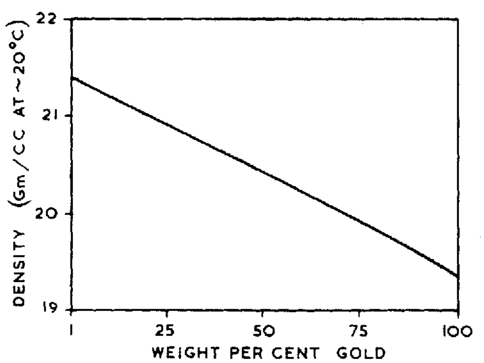

Fig. 16 Density curve of quenched gold-platinum alloys (37)

parameter curve for quenched single phase alloys (37). Fig. 17 provides the essential thermal conductivity and magnetic susceptibility data for alloys at 18°C. Although gold additions initially decrease the thermal conductivity of platinum, the curve rapidly levels out and remains almost constant at a value of about 0.25 watts/cm./degree over the composition range 25 to 70 per cent of gold (10). The conductivity then rises rapidly to that of pure gold. It is now known that the intermediate alloys on this curve could not all have been quenched from the single phase region and it is probable that the true thermal conductivity of single phased alloys containing 40 to 50 per cent of gold is lower than the values indicated.

Small quantities of gold rapidly reduce the paramagnetic properties of platinum, but after 10 per cent has been added the change becomes more gradual. (10). The susceptibility of quenched single phase alloys varies continuously with composition, and becomes zero for a gold content of 74 per cent. The susceptibility of alloys quenched from lower temperatures varies with gold content in a linear manner over the duplex region.

Melting and Working Practice

The alloys are generally induction melted in air in zircon crucibles, ingots being cast into moulds of graphite or water-cooled copper (45). However satisfactory the casting operation, the characteristics of the system ensure a tendency towards inverse segregation and industrial working procedures, although varying considerably in detail, are all designed to promote efficient homogenisation. The coarse dendritic structure is preferably broken down by hot forging or rolling, after which long soaking periods are required to eliminate small areas of platinum-rich metal.

The whole range of alloys can be cold worked after quenching from temperatures not higher than 1000°C. The most ductile material is achieved by annealing at 1000°C, after which the temperature can be slowly dropped before water-quenching from 850°C.

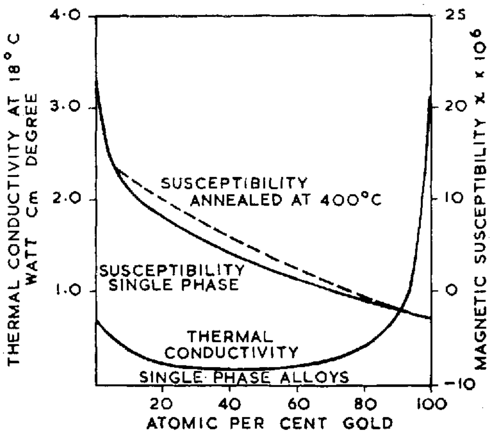

Fig. 17 Thermal conductivity and magnetic susceptibility data at 18°C for quenched gold-platinum alloys (10)

Although the difficulty of working increases with platinum content up to 80 per cent, even this alloy can be easily worked after a reduction in thickness of 50 per cent. As the final properties of the resultant rod and sheet reflect the entire thermal and mechanical history of the material, casting and working procedures require very careful control.

Interesting dimensional changes result during the heat treatment of gold-platinum alloys which have been insufficiently homogenised. This behaviour was first reported by Holzmann (47). Drawn 70/30 gold-platinum rods were found to shorten by as much as 9 per cent when heated for 1 hour at 1100°C. The effect became less pronounced as the specimen diameter decreased. Specimens produced from ingots which had been very slowly solidified contracted less than those from chill-cast ingots and extremely slow rates of heating tended to diminish the extent of dimensional change. The shrinkage is attributable to the more or less rapid elimination of strong concentration gradients during heat treatment.

Resistance to Oxidation and Corrosion

Gold volatilises at a negligible rate in oxygen, platinum evaporates readily. The evaporation curves of gold-platinum alloys as obtained by Raub and Plate (48) illustrate the basic characteristics of this system in a striking manner. Fig. 18 shows that small additions of gold to platinum initially decrease the evaporation rate fairly rapidly. Over the duplex region, however, the evaporation rate remains fairly constant, suggesting that the composition of vapour in equilibrium with the two phases is independent of their relative volumes. Only when the platinum-rich phase has disappeared does the gold reduce sensibly the rate of volatilisation. Duplex alloys which have been soaked at about 1200°C for several days in air frequently show thin surface layers of a gold-rich alloy when microscopically examined (37). This behaviour is probably a consequence of preferential evaporation from the platinum-rich phase in which platinum diffuses very slowly (33).

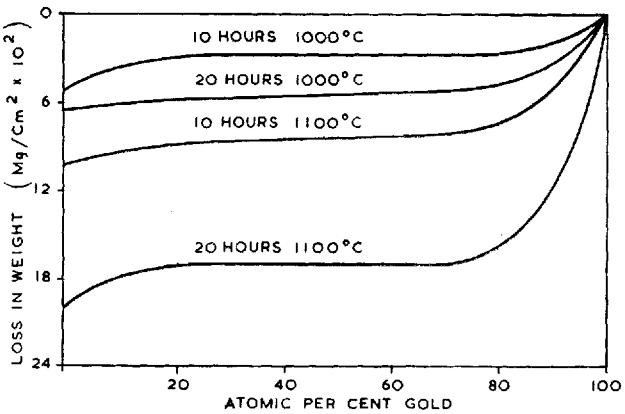

Fig. 18 Effect of composition upon the rate of volatilisation of gold-platinum alloys heated in a current of oxygen (48)

The alloys, very resistant to corrosion by most acids are dissolved fairly rapidly by aqua regia. Cyanide solutions dissolve the gold-rich alloys rather more slowly. The complete resistance of the gold-rich alloys to simultaneous attack by sodium sulphate, sulphuric acid, and caustic soda is demonstrated by their prolonged employment in the viscose rayon industry.

Klochko and Nikitina (49) reported on the anodic behaviour of the system in 1955. Experiments in which a 1N solution of chlorauric acid was used as an electrolyte showed that alloys annealed by cooling from 1000°C in air over a period of 12 days were very much more negative with respect to gold than quenched alloys. Plateaus on both sets of e.m.f. curves agreed with the width of the duplex region corresponding to the metallurgical condition of the specimens. Anodic solubility tests carried out in a 5N solution of HCl showed that the gold-rich phase was always the first to go into solution. With all duplex alloys the dissolved part of the anode had the composition of the limiting gold-rich solid solution. Quenched and slowly cooled alloys both dissolved at roughly the same rate, which remained fairly constant at about 0.2 to 0.3 gm/cm²/amp-hour across the entire duplex region. The solubility of the platinum-rich solid solution compared to that of the duplex alloys was very low indeed.

Applications

Gold-platinum alloys are now primarily used as spinning jets in the viscose rayon industry (50) where they withstand corrosive conditions for long periods. Due to the abrasive action of the alkaline viscose solutions which may contain titanium dioxide (40) mechanical conditions are also severe. Heat treatable alloys are preferred, as the perforation process can be performed on soft solution treated material which is subsequently aged to develop its full mechanical properties. A high hardness also facilitates the maintenance of the polished surface so desirable on the outlet faces of these spinning jets. Alloys containing 50 to 85 per cent of gold are employed. While the 70/30 gold-platinum alloy is very widely used special conditions frequently justify the use of alloys containing 40 to 50 per cent of platinum, which have a longer working life (39, 43, 46). The beneficial effects of small additions of rhodium to spinning jet alloys have already been discussed.

Platinum hardens gold considerably, and laboratory utensils containing 5 and 10 per cent of platinum are frequently used for operations which do not require a more expensive or refractory alloy. Crucibles of the 10 per cent platinum alloy are, for example, very suitable for the ashing of flour and other phosphorus-containing organic materials (51). Although equal to pure platinum in its resistance to hydrofluoric and other acids, fused alkalis and sodium carbonate, the ten per cent platinum alloy is inferior with respect to aqueous or fused cyanides and fused nitrate mixtures. It can, like platinum, be readily fused with soft glass (58).

Platinum-rich alloys are also used in the laboratory. Platinum crucibles alloyed with a few per cent of gold have a higher strength than pure platinum at 1000°C, a finer grain structure, better shape stability and lower weight losses when used for a variety of analytical operations (53). Platinum-gold alloys are more readily soft soldered than pure platinum or iridium-platinum. This was once considered a factor of some importance although in these days of refined laboratory techniques the use of soft solder on platinum alloys cannot be recommended.

Films of gold-platinum alloys are applied to non-conducting substrates for a variety of purposes. Deposits are achieved by sputtering or by using a metallising paint. Sputtered films ranging in thickness from 75–2000 Å can be applied to soft glass, borosilicate glass, alumina, silica and other refractories. The temperature coefficient of sputtered films is not greatly affected by thickness, being about 0.0004 per °C over the range 25 to 600°C (54).

Thicker deposits, achieved by firing on metallising preparations are being increasingly used for the production of stable, non-oxidisable resistors suitable for high temperature operations. Films having electrical resistivities of 20 to 50 ohms per square have temperature coefficients of about 0.0003 per °C. Thicker films have very much higher, and thinner films very much lower temperature coefficients (55).

Photographic methods of achieving meandering resistance paths have been developed, and these portions of the resistance over which sliding contact occurs can be suitably reinforced. The wear on such paths is very low, resistance changes being of the order of 0.6 per cent after 300,000 operations under a 4 g/load. Resistance noise values from 70° to 550°K are within the range 0.013 to 0.003 uV/V. Abrasion techniques can produce patterns having resistances of 5 million ohms within a 2 inch diameter circle (56). Elements of even higher resistance are achieved by winding alloy coated glass fibres around cylindrical formers (57).

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