A High Strength Gold Alloy for Use at High Temperatures

Roger Lacroix and Claude Niney

Comptoir Lyon-Alemand Louyot, Paris

By the addition of 15 per cent platinum and 1 per cent rhodium to gold a two-phase alloy is obtained whose mechanical properties both at high and at normal temperatures are superior to those of fine gold. This alloy provides a possible substitute for platinum for applications involving corrosive conditions at temperatures up to 800°C.

In its resistance to chemical attack and the ease with which it can be fabricated gold may be compared with platinum. Its greater availability and lower price would make it into a serious competitor if it were not for its much lower melting point and its relatively poor mechanical strength. These preclude its use for many industrial applications. Might it not be possible, however, to create gold alloys of greater strength and higher melting point without sacrificing its other advantages? The possibility of raising the melting point by a significant margin is unlikely; on the other hand there is no reason why the mechanical properties of gold should not be improved to enable it to compete with platinum within a temperature range between room temperature and, say, 800°C.

The hardness, tensile strength and durability of gold have in many cases been improved by the addition of base metals such as copper, nickel and zinc. The great variety of alloys thus obtained still shows satisfactory corrosion resistance for the majority of applications in the jewellery industry, in dentistry and in electronics, but this resistance falls short of requirements either if the temperature is raised above 300 to 500°C or if the metal is subjected to a particularly heavy combination of chemical and mechanical attack, as for example with bushings for synthetic textile fibres.

The chief reason for the failure of alloys containing base metals to stand up to aggressive conditions at high temperatures is the deterioration of the base metals at the surface of the alloy. Their loss by oxidation or corrosion causes diffusion of the base metal from the interior towards the impoverished surface areas. If corrosion and consequent diffusion continue, at least in theory, the base metals contained in the alloy can be eliminated. To avoid this drawback and at the same time to improve the mechanical properties of gold it becomes necessary to limit the alloy constituents to the most resistant of the noble

metals—the platinum group metals—and their percentages must be kept to a minimum in order to retain price advantage.

Considerable research has already been devoted to the systems formed by gold with metals of the platinum group (1). Alloyed with palladium, gold forms a continuous series of solid solutions, the hardness of which does not exceed 50 Vickers.

The solubility of iridium and rhodium in gold in the solid state is very limited. Rudnitskii and his colleagues (2, 3) have measured the solubility of both iridium and rhodium, and E. Raub and C. Falkenburg (4) that of rhodium. The solubility of iridium is less than 0.1 per cent, while that of rhodium follows a pattern:

at 1000°C 1.4 atomic per cent = 0.7 per cent by weight
at 800°C 1.1 atomic per cent = 0.6 per cent by weight
at 600°C 0.4 atomic per cent = 0.2 per cent by weight

In molten gold this solubility becomes significant only at temperatures where the usefulness of gold becomes problematical and where, moreover, the two metals show a strong tendency to segregate. As a result, it is not possible to achieve alloys with a high gold content combined with long life.

The solubility of ruthenium and osmium in gold is practically nil.

The platinum-gold system is the most promising. Numerous investigations have shown its value, and a good summary of the system has been given by A. S. Darling (5). Gold and platinum form an unbroken series of solid solutions showing a large miscibility gap in the solid state. The structural transformations in the solid state caused by this phenomenon enable very great hardnesses to be achieved, particularly in cases where the gold content varies between 20 and 60 per cent. Small additions of gold generally increase the hardness of platinum to a significant degree, whereas small additions of platinum have little effect on gold. The need to turn

Crucibles made in the 84 per cent gold, 15 per cent platinum, 1 per cent rhodium alloy OPR 1 have been successfully used for melts of halide salt mixtures with melting points ranging from 620 to 720°C

to alloys with a high platinum content, and the need for precision in carrying out mechanical operations and heat treatment in order to obtain satisfactory results in respect of hardness and other properties all combine to show that binary platinum-gold alloys are not a satisfactory solution to the problem of how to increase the mechanical strength of gold. Having abandoned the idea of binary alloys of gold with one of the platinum metals, one turns to ternary alloys.

While almost insoluble in gold, rhodium and iridium are soluble in platinum in any proportion, at least under normal conditions. One may therefore expect that by adding these metals to gold-platinum alloys, Pt-Ir or Pt-Rh phases are formed which are less soluble than platinum, thus increasing the extent of the dissociation zone of the platinum-gold system. One may likewise expect that the addition of platinum to gold would improve the solubility of iridium and

The microstructure of alloy OPR 1 cold rolled and annealed for 30 minutes at 700°C (left) and after cold rolling. $\times 600$

Mechanical Properties of the Alloy
Au 84%-Pt 15%-Rh 1%

	<i>Annealed</i>	<i>Cold Worked</i>
Vickers Hardness	70-85	120-140
Ultimate Tensile Strength, kg/mm ²	25-30	42-48
Elastic Limit, kg/mm ²	12-17	40-45
Elongation per cent	25-30	0-4

rhodium. This is borne out by the work of E. Raub and G. Falkenburg (4) on the platinum-gold-rhodium system. If the rhodium content is kept below 1 per cent, say between 0.1 and 0.6 per cent according to the platinum content, the resulting alloys may be precipitation hardened. Such alloys have been tested by E. Grafried and his colleagues (6) for producing bushings for synthetic textile fibre.

An alloy for bushings consisting of 70 per cent gold, 29.8 per cent platinum and 0.2 per cent iridium by weight has also been the subject of a patent (7).

Since gold is not wetted by molten glass, gold-rhodium-platinum alloys have also attracted a great deal of interest. Being primarily intended for the glass industry, research has centred on high melting alloys—rhodium-platinum alloys with small additions of gold (8, 9). Their usefulness has remained limited due to the fugacity of gold. Its evaporation may lead to premature cracking of apparatus and its dissolution in certain glasses produces in the latter an undesirable rosy tint or affects their mechanical properties.

For applications at temperatures below 850°C, particularly in the preparation of single crystals from alkaline halides and fusible mixtures of halogenated salts, we turned to rhodium-platinum-gold alloys with a high gold content. The problem may be expressed as follows:

“From an economic angle, what are the minimum quantities of rhodium and platinum one would need to add to gold in order to obtain an alloy that is simple to produce, ductile, easy to fabricate and suitable for crucibles of adequate durability at 700°C with occasional fluctuations up to 800°C?”

The best solution to this problem is given by an alloy called OPR 1 of the following composition by weight:

Gold	84 per cent
Platinum	15 per cent
Rhodium	1 per cent

The Alloy and Its Properties

The alloy OPR 1 is easy to prepare by melting in a refractory crucible of alumina, zirconia, magnesia, or graphite with no special precautions. The rhodium dissolves rapidly in the molten platinum-gold mixture at a temperature of 1400°C maximum. The cast ingots may be rolled, with a reduction of thickness of up to 400 per cent.

The alloy consists of two phases; a gold-rich matrix and a finely dispersed gold-rhodium-platinum phase, as shown in the photomicrographs. The two phases belong to the face centred cubic system with parameters $a=4.06$ and $3.88 \text{ \AA}$.

The mechanical properties of alloy OPR 1 after annealing for 30 minutes at elevated temperatures

Its density at 20°C is 19.58 g/cm³, its melting range 1175 to 1315°C, and its coefficient of linear expansion between 20° and 800°C 12.7×10^{-6}

Mechanical Properties at Room Temperatures

The table on the facing page shows the mechanical properties of the alloy in the fully annealed and the cold worked conditions. The graph below it shows how these properties vary with temperature when annealed for 30 minutes.

High Temperature Mechanical Properties

Values for the mechanical properties of the alloy at various temperatures are shown in the graph alongside. These were obtained by accelerated tensile tests. At 700°C, for instance, we find:

Ultimate tensile strength	6 kg/mm ²
Elastic limit	4 kg/mm ²
Elongation	45 per cent

High temperature tensile tests were carried out using cylindrical test pieces 1.5 mm in diameter with a gauge length of 50 mm. When stressed in a constant tension of 300 g/mm², failure occurred at 800°C after a period of at least 300 hours, and at 900°C at the end of 40 hours. Elongation in both cases was in excess of 70 per cent.

Resistance to Corrosion

As would be expected, the alloy shows an exceptionally good resistance to corrosion. No variation

in weight was observed on specimens having a surface area of 4 cm² under the following conditions:

Immersion for 25 days in:

Nitric acid (d=1.38) at 80°C

Sulphuric acid (d=1.83) at 80°C

Hydrochloric acid (d=1.19) at 80°C

Immersion for 80 days in the same acids at 20°C.

Nor was the alloy attacked in any way by hydrogen sulphide either as gas or in solution.

A crucible in alloy OPR 1 for the continuous fusion of molten salt mixtures containing aluminium fluoride. Operating in the range 650 to 750°C, the crucible has a life of up to six months. The associated thermocouple sheath is also made in OPR 1 alloy

It is likewise resistant to fused halides up to 800°C. Above this temperature, crucibles deteriorate rapidly, chiefly through creep.

Applications of the New Alloy

The alloy can readily be rolled and drawn, and it can be deep-drawn and cupped without difficulty, it can be brazed to itself, or it can be brazed by a torch and oxygen-town gas, using fine gold as the filler metal.

It has been used for bushings for synthetic textile fibres in the presence of hydrogen sulphide at 50°C.

The illustration on page 95 shows various laboratory crucibles with capacities from 30 to 75 ml. They were used to melt caesium iodide (621°C), sodium iodide (653°C) as well as eutectic mixtures of sodium fluoride and lithium fluoride (61 per cent LiF, melting point 652°C) and lithium fluoride/magnesium fluoride (53 per cent LiF, melting point 718°C).

The illustration on page 97 shows a crucible 61 cm long and the sheath of the associated thermocouple. It is used for the continuous fusion at 650 to 750°C of molten aluminium fluoride based salt mixtures. It has a life of up to six months.

References

- 1 V. A. Nemilov, T. A. Vidusova, A. A. Rudnitskii and M. M. Putsikina, *Akad. Nauk. USSR, Izv. Sek. Plat.*, 1946, 176-224
- 2 A. A. Rudnitskii and V. P. Polyakova, *Zh. Neorg. Khim.*, 1959, 4, (10), 2304-2307
- 3 A. A. Rudnitskii and A. N. Khotinskaya, *Zh. Neorg. Khim.*, 1959, 4, (11), 2518-2524
- 4 E. Raub and G. Falkenburg, *Z. Metallkunde*, 1964, 55, (7), 392-397
- 5 A. S. Darling, *Platinum Metals Rev.*, 1962, 6, (2), 60
- 6 E. Grafried, K. Protzmann, K. Ruthardt and H. Speidel, 100 Jahre Heraeus, Hanau, 1951, p. 43
- 7 Johnson Matthey, *British Patent* 1,112,766, 1966
- 8 G. L. Selman, M. R. Spender and A. S. Darling, *Platinum Metals Rev.*, 1965, 9, (3), 92
- 9 G. L. Selman, M. R. Spender, A. S. Darling, *Platinum Metals Rev.*, 1966, 10, (2), 54

Humidity Control Equipment

GOLD GRIDS IN ELECTRONIC HUMIDISTATS

Precise control of humidity is needed in buildings as diverse as offices, hospitals, schools, greenhouses, and textile plants. Humidistats for these purposes must offer fast response and close control of the relative humidity in a room by continuous sensing and appropriate operation of humidification or dehumidification equipment to the required level of relative humidity. Two new models have recently been developed by Honeywell's Commercial Division at Arlington Heights. They are three inches high, two inches wide and one and a half inches deep, and are thus suitable for wall mounting almost anywhere or can be modified for mounting on ducting.

Whereas the new pneumatic model is used for extensive control systems or where there is a danger of explosion, the new electronic model humidistat is suitable for smaller systems or where really fast and accurate response down to 1 per cent relative humidity is essential. The Mikronik electronic humidistat uses a sensing element consisting of a thin plastic wafer covered with two grid patterns of gold lines and coated with lithium chloride, which is very sensitive to moisture. The grids are connected to separate terminals. When the humidity increases the area between the grid patterns becomes more conducting so that slightly more current flows from one to the other. This current, when amplified, operates the humidity control equipment.

Although these elements are so compact, each gold grid line is more than two feet long to give high

sensitivity and good response. Gold was chosen because of its high conductivity and excellent resistance to corrosive atmospheres. A dozen different sensing elements are available to cover relative humidity ranges from 5 to 95 per cent. To change the range of operation it is only necessary to pull out one element and plug in the one required.

The Mikronik electronic humidistat made by Honeywell incorporates a sensing element consisting of a plastic wafer with two gold grids on its surface. The element is mounted on the device as shown and is inserted within the slim case. The humidistat is suitable for the control of relative humidity in a wide variety of situations