The Wetting of Platinum and its Alloys by Glass

III - MICROSTRUCTURE AND MECHANICAL PROPERTIES OF GOLD-RHODIUM-PLATINUM ALLOYS

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In the concluding part of this study of platinum alloys for use in the glass industry, correlations between structure, composition and high temperature mechanical properties have been obtained in the platinum-rich corner of the gold - rhodium - platinum system. Although gold additions decrease the melting point of rhodium-platinum alloys, the effect is not pronounced. The alloy containing 5 per cent gold and 10 per cent rhodium which was shown in the previous parts of the paper to be particularly resistant to wetting has a solidus between 1730°C and 1760°C. This alloy is single phased at temperatures above 1100°C and is more resistant to creep than the 10 per cent rhodium-platinum solid solution. Some of these improved high temperature properties are sacrificed if the gold content is reduced to 3 per cent.

Small additions of rhodium to gold-platinum alloys are known to broaden the miscibility gap (1), which eventually interacts with the solidus to produce a system of the peritectic type (2, 3). The only information on alloys containing substantial quantities of rhodium comes from Raub and Falkenburg (4), who published the results of their X-ray determinations in 1964. The 800°C isotherm, taken from this work, is shown in Fig. 1. At this temperature level 1 per cent by weight of rhodium completely eliminates the single-phase region at the gold-rich end of the diagram. Although gold also reduces the solubility of rhodium in platinum, the effect is not so pronounced and the platinum-based solid solutions extend in an unbroken line over a considerable area of the diagram.

The present investigation has extended the field of study to higher temperature levels. Although attention has been confined largely to those platinum-rich alloys, described in an earlier paper (5), which are reluctantly wetted by molten borosilicate glass, a great deal of basic information has come to light. The creep properties have been related to composition, and it has been shown that high temperature strength is not incompatible with resistance to wetting by molten glass.

Alloy Preparation

Platinum and rhodium sponges, and gold grain, all of the highest available purity, were induction melted, in air, in alumina crucibles before being chill cast into thick copper moulds. The ingots were homogenised at 1250°C for periods up to 64 hours, slowly cooled to 800°C and held at this temperature for 16 hours before quenching into water. After this treatment all the alloys studied

Fig. 2 3 per cent gold-12 per cent rhodium-platinum quenched after annealing for 48 hours at 900°C (×500)

Fig. 3 5 per cent gold-10 per cent rhodium-platinum quenched after annealing for 24 hours at 900°C (×500)

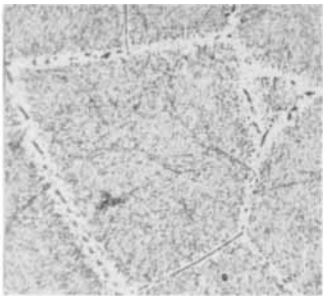

Fig. 4 13 per cent gold-2 per cent rhodium-platinum quenched after annealing for 24 hours at 900°C (×500)

could be cold worked into sheet or wire, although it was noted that the ease of working declined rapidly when the gold content exceeded 5 per cent.

The total base metal impurity content of the alloys was of the order of 0.005 per cent. Cold rolled sheet examined after the final stage of fabrication contained typically the following impurities:

Cu 0.001%, Ca 0.0005%, Cr 0.001%,
Fe 0.002%, Mg 0.0002%, Pd 0.001%

Metallographic Studies

Solidus determinations were undertaken by the "bracketing" method, a 20 per cent rhodium-platinum : 40 per cent rhodium-platinum thermocouple being employed because of the high temperatures involved.

Samples of homogenised and rolled sheet were rapidly heated, in intimate contact with this thermocouple, to a temperature 20°C below the desired level, held constant for one hour and then taken up to the quenching temperature at a rate of 20°C per hour. Quenching was accomplished in water from a vertical furnace, and the quenching temperature was increased by increments of 20°C until signs of fusion became apparent in polished and etched microsections.

Attempts were also made to determine by metallographic methods the boundary between the homogeneous and two-phase regions. This was found to be rather an approximate technique in view of the steeply sloping nature of the boundary curve. Alloys containing more than 7 per cent of gold were, moreover, very highly stressed by rapid quenching. Grain boundary precipitation was not completely suppressed and this led to what might almost be described as stress corrosion. In some instances etching removed

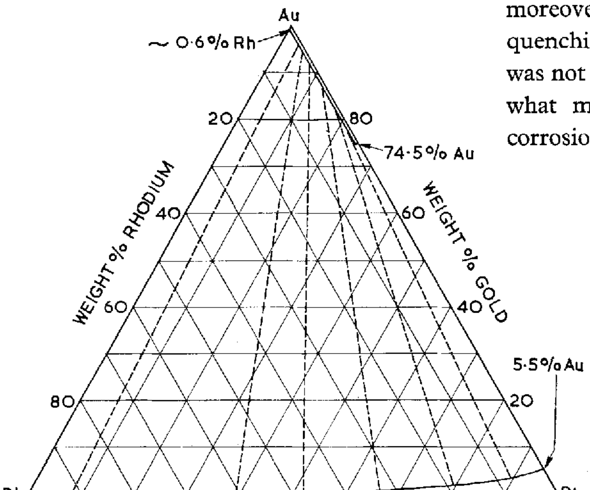

Fig. 1 Isothermal section through the gold-rhodium-platinum constitutional diagram at 800°C (after Raub and Falkenburg (4))

Fig. 5 5 per cent gold-10 per cent rhodium-platinum quenched after annealing for 24 hours at 1200°C (×500)

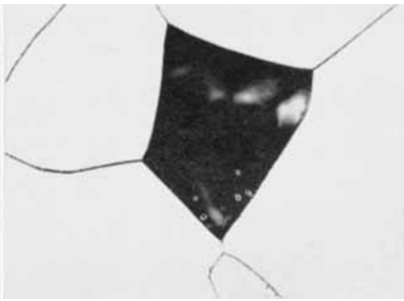

Fig. 6 13 per cent gold-2 per cent rhodium-platinum quenched after annealing for 24 hours at 1200°C (×500). Note incompletely suppressed precipitate round the grain boundaries and the cavity left by a grain detached by etching

complete grains from the surface of polished microsections, and this behaviour complicated the search for small quantities of a second phase at the grain boundaries.

Figs. 2, 3 and 4 show typical microstructures of the alloys containing 3, 5 and 13 per cent by weight of gold after quenching from 900°C. At this temperature the phase boundary evidently occurs between 3 and 5 per cent of gold. Duplex structures are shown in Figs. 3 and 4. Globular precipitates of the gold-rich phase can be distinguished round the grain boundaries of these microsections, while the constituent in the body of the grains is too fine for complete resolution. The gold denuded zones round the grain boundaries and the tendency towards subgrain formation are characteristic features of the structure of alloys heat treated at this temperature level.

The homogeneous structures shown in Figs. 5 and 6 were obtained by quenching from 1200°C. The well-defined cavity shown in Fig. 6 occurred when a complete grain fell out of the surface during the process of etching.

X-ray Diffraction Work

Filings taken from homogenised alloys were sealed in silica quills and heat treated at the same time as the metallographic specimens. After rapid quenching, these filings were used for X-ray diffraction studies with Cu Kα radiation and a Phillips powder camera. The patterns obtained were those of either a

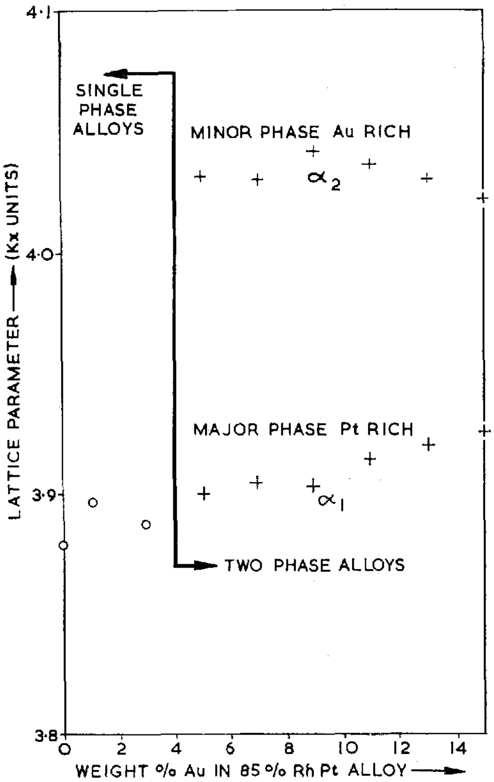

Fig. 7 Lattice parameters of the phases present in ternary gold-rhodium-platinum alloys quenched after annealing for 24 hours at 850°C

homogeneous face centred cubic solid solution or of a mixture of two such phases. The lattice parameters of the phases present in alloys quenched from 850°C are plotted in Fig. 7. These results confirmed the sudden emergence of the gold-rich phase when the gold content exceeded 3 per cent by weight. They agreed closely with values obtained by Raub and Falkenburg (4) at 800°C, but they did not permit an accurate determination of the whole phase boundary.

Resistometric Studies

The boundary between the single- and two-phase regions was finally determined by electrical resistance methods. The differential resistance bridge employed was first described by Stockdale (6), with modifications by Haughton (7). Two test specimens of very similar temperature/resistance characteristics were connected in opposition, the platinum leads having resistances which were low compared to those of the test specimens.

In general, the "standards" used for this work were the 15 per cent gold-platinum alloy and the 3 per cent gold, 12 per cent rhodium-platinum alloy. The test specimen and an appropriate "standard" were placed in a horizontal tube furnace, in a region of uniform temperature which was adjusted to about 700°C. The bridge was then balanced as closely as possible, and the furnace temperature changed by increments of 30°C at half-hourly intervals. The out of balance e.m.f. corresponding to each temperature level was carefully measured with a vernier potentiometer. A typical example of the graphs obtained by plotting these millivolt readings as a function of temperature is provided in Fig. 8. The lower inflection on this curve is caused by the 3 per cent gold, 12 per cent rhodium-platinum alloy "standard" entering the single-phase region. The upper inflection is attributable to the test specimen undergoing the same transformation.

At least three sets of determinations were made on each alloy, and the results obtained defined the position of the phase boundaries

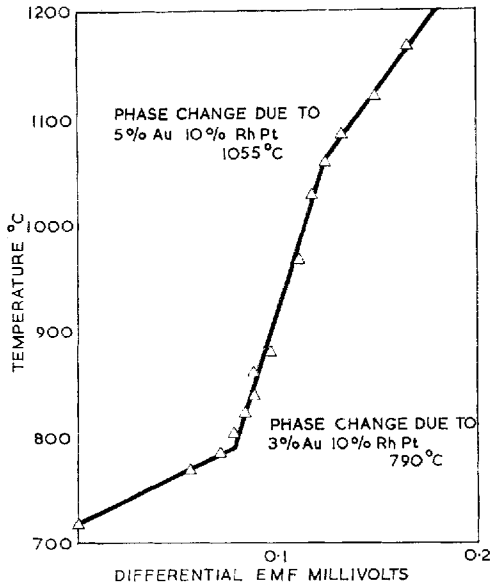

Fig. 8 Typical curve obtained with the differential bridge

involved within limits of ±20°C. Support for the accuracy of these resistometric determinations was provided by the close agreement between the value of 1028°C determined for the 15 per cent gold-platinum alloy and the established value of 1030°C (8). Similarly, the value of 790°C determined by the resistance bridge on the 3 per cent gold, 12 per cent rhodium-platinum alloy is close to the 800°C obtainable from the X-ray work of Raub and Falkenburg (4).

Section through the Diagram at 85 per cent of Platinum

The results obtained by application of the previously described techniques made it possible to construct the vertical section shown in Fig. 9. It is obvious from this diagram that alloys used in contact with molten borosilicate glass will all be working in the single-phase condition. Differences in contact angle behaviour cannot therefore be attributed to discontinuous microstructural changes and must therefore be caused by fundamental modifications in the nature of the solid solution induced by increasing quantities of gold.

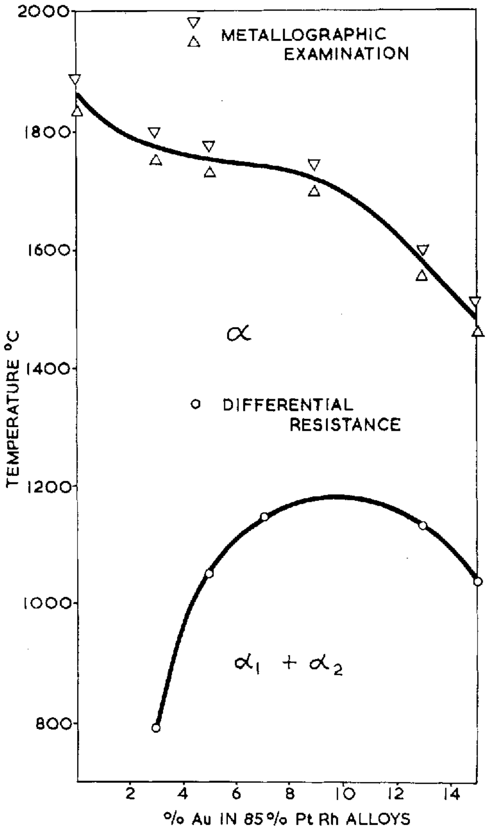

Fig. 9 Vertical section through the gold-rhodium-platinum constitutional diagram on a parallel traverse at 85 per cent of platinum

High Temperature Mechanical Properties

Stress-rupture data for the alloys containing 3 and 5 per cent of gold are presented in Fig. 10. These tests were made on specimens machined out of rolled sheet 0.060 inch thick and 0.25 inch wide. The gauge length was 1.5 inch. When stressed in tension at 700 p.s.i. at 1400°C the 5 per cent gold, 10 per cent rhodium, 85 per cent platinum alloy resists failure for approximately 150 hours. This compares with 60 hours for the binary 10 per cent rhodium-platinum alloy and 0.5 hour for pure platinum tested under the same conditions. The 3 per cent gold, 10 per cent rhodium, 87 per cent platinum alloy has a slightly shorter test life than the 10 per cent rhodium-platinum alloy although the difference is not pronounced. As shown by the elongation curves on Fig. 11, the gold-bearing alloy creeps less rapidly than the binary rhodium-platinum alloy, and although it has a lower elongation at fracture, this is unlikely to have an adverse effect upon its performance in service.

All the gold-bearing alloys were found to fail at the grain boundaries after high temperature stressing. This behaviour occurred at all stress levels, although rhodium-platinum is perfectly ductile at stresses above 400 p.s.i. at 1400°C. At lower temperatures, however, the 10 per cent rhodium-platinum alloy frequently exhibits intercrystalline failure and this has not imposed any restrictions upon its industrial employment.

Components in the glass industry are invariably taken out of service when distortions prevent efficient operation of the process. As

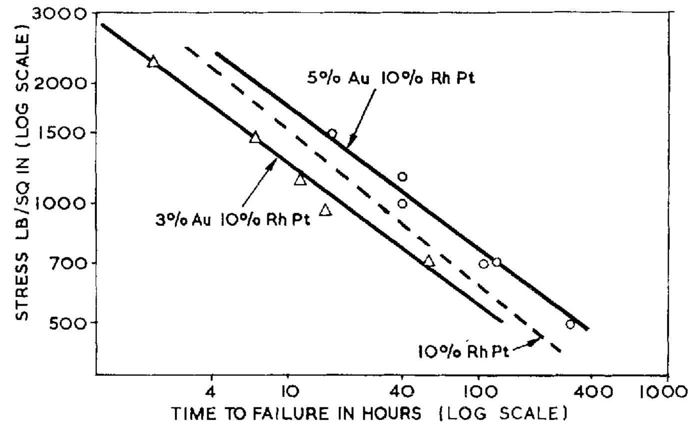

Fig. 10 Stress-rupture data for two gold-rhodium-platinum alloys tested at 1400°C. The broken line represents the performance of the binary 10 per cent rhodium-platinum alloy at the same temperature

indicated by the table, the fracture elongations of the gold-bearing alloys at 1400°C are high enough to ensure appreciable ductility under industrial conditions.

Fracture Elongations of Gold-Rhodium-Platinum Alloys at 1400°C

Stress Level lb./sq. in.	3% Au-10% Rh-Pt	5%Au-10% Rh-Pt
750	27%	25%
1025	19%	27%
1167	50%	42%
1500	53%	45%

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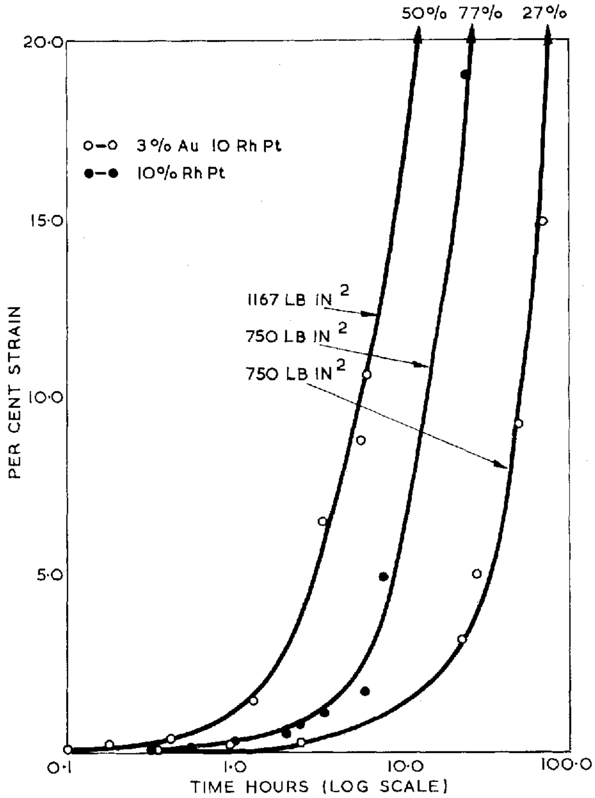

Fig. 11 Creep curves of the 3 per cent gold-10 per cent rhodium-platinum alloy and of the binary 10 per cent rhodium-platinum alloy tested at 1400°C

Electrodeposition of Iridium

PROGRESS IN DEPOSITION FROM AQUEOUS SOLUTIONS

A recent paper by C. J. Tyrrell of International Nickel Limited (*Trans. Inst. Metal Finishing*, 1965, **43**, 161–6) proposed a bromide electrolyte for the deposition of iridium from aqueous solution. The electrolyte contains 5 g/l of iridium as the bromide and 8 g/l of hydrogen bromide. It is operated at 75°C at a cathode current density of 0.15 amp/sq.dm to give deposits which are crack-free to a thickness of 1 μ. Further deposition will produce cracked deposits, but nevertheless the coating remains smooth and bright to a thickness of 10 μ.

Dr Tyrrell also reports on his experiences with iridium chloride electrolytes, where he was unable to confirm the cathode efficiencies obtained by earlier workers. However, these variations may be explained by the work of G. A. Conn of Westinghouse Electric (*Plating*, 1965, **52**, (12), 1258). This author has found that the cathode efficiency of an iridium chloride electrolyte is markedly improved by increased anodic current density, and also by the introduction of auxiliary a.c. electrodes. When these electrodes were operating at a current density of 50 amp/sq.dm a.c. the cathode efficiency improved from 2 to 30 per cent. The maximum thickness obtained in these tests was 25 μ, and again cracking occurred with the heavier deposits.

Thus, while it appears that for thick crack-free deposits the fused cyanide electrolyte is still the only practical plating system, progress is being made with aqueous electrolytes, and thin coatings are now possible from stable aqueous electrolytes. J. H.