The Wetting of Platinum and Its Alloys by Glass

II—RHODIUM-PLATINUM ALLOYS AND THE INFLUENCE OF GOLD

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In the second part of this paper it is shown that rhodium-platinum alloys are less readily wetted by glass than pure platinum, although the effect is marginal and disappears at temperatures above 1200°C. Gold additions are shown to increase the resistance to wetting much more effectively, the equilibrium contact angle between borosilicate glass and platinum containing 5 to 7 per cent of gold and 10 per cent of rhodium remaining above 75° up to 1500°C. This ternary alloy is stronger and more resistant to creep at high temperatures than the binary 10 per cent rhodium-platinum alloy.

Rhodium-platinum alloys, being extensively used for the bulk handling of molten glass, are generally believed to be less readily wetted by glass than pure platinum. Support for this belief was provided by Dietzel and Coenen (1) who studied the effect of rhodium content upon the equilibrium contact angle in air and confined their investigations to soda glass and to temperatures below 1050°C.

Pure gold is known to resist wetting by glasses which melt below 1063°C (2). Gold-platinum alloys, although melting at higher temperatures than pure gold, have inadequate mechanical properties under the conditions commonly encountered in glass manufacture. The present investigation has shown that small quantities of gold, added to rhodium-platinum alloys, greatly increase their resistance to wetting by borosilicate glasses without deleterious effects upon their high temperature strength or chemical inertness.

Alloy Preparation

Binary rhodium-platinum alloys, covering the composition range from platinum to rhodium in eight increments, were made up in the laboratory. Those containing more than 20 per cent of rhodium were melted in the argon arc furnace. The remainder were induction melted in alumina crucibles in air. The ingots were homogenised close to the melting point, hot forged, and finally cold rolled to sheet.

The gold-platinum and gold-rhodium-platinum alloys were induction melted in air, being then cast into square section ingots in a copper mould. These ingots were homogenised at 1130°C for periods ranging from 16 to 64 hours, slowly cooled to 800°C and held at this temperature for 16 hours before quenching in water. This treatment produced ductile ingots which could be cold rolled to sheet with little difficulty.

Dewetting Effects

In the previous report (3) the dewetting effects observed when beads of borosilicate glass were heated on pure platinum at temperatures above 1200°C were interpreted in terms of the shape of the "initial" equilibrium

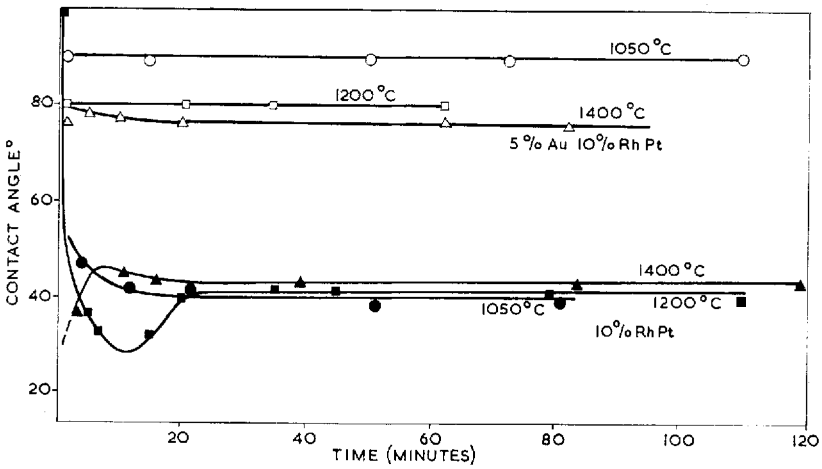

Fig. 1 Curves showing the effect of time on the contact angle between "E" glass and two platinum alloys maintained in air at constant temperature

contact angle curve. The results of this recent series of tests have confirmed that alloys behave in a similar manner to the pure metal. The effect is well illustrated by the curves plotted on Fig. 1 which contrasts the differing behaviour of alloys with and without a 5 per cent addition of gold. Beads of "E" borosilicate glass heated on 10 per cent rhodium-platinum at 1200°C and 1400°C exhibit strong retraction effects during the approach to equilibrium. At 1050°C no dewetting occurs and these relationships agree with the shape of the curve for the 10 per cent rhodium-platinum alloy in Fig. 2, which shows that the "initial" equilibrium contact angle passes through a minimum at 1130°C.

None of the alloys containing gold, or more than 10 per cent of rhodium, had this minimum in their contact angle curve, and these alloys showed no tendency to "dewet" when observed in the hot stage microscope.

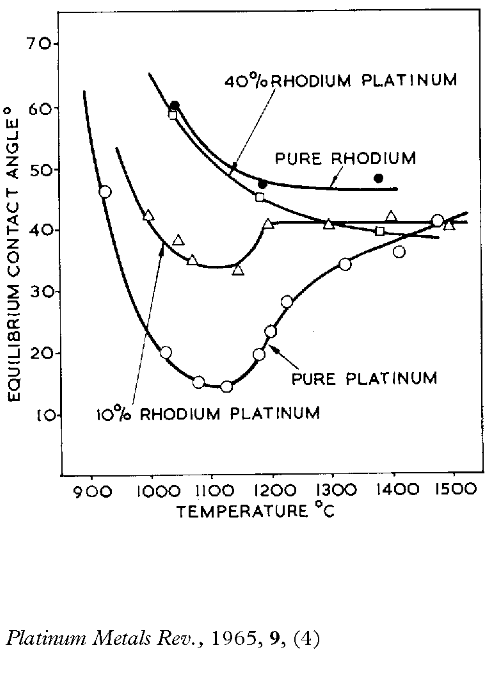

Fig. 2 The effect of temperature on the equilibrium contact angle of "E" glass on rhodium-platinum alloys heated in air. Although rhodium increases the contact angle considerably at lower temperatures, the increase becomes marginal even with very high rhodium contents above 1200°C

Rhodium-Platinum Alloys

These experiments were undertaken to confirm the work of Dietzel and Coenen (1), who found that the alloy exhibiting maximum resistance to wetting in air contained approximately 40 per cent by weight of rhodium.

Contact angle determinations were made on eight alloys covering the full composition range. The effect of temperature upon the contact angle of the "E" glass melted in a number of alloys is shown in Fig. 2, in which curves relating to alloys containing more than 40 per cent of rhodium have been omitted for reasons of clarity. The figure shows that although rhodium additions increase the

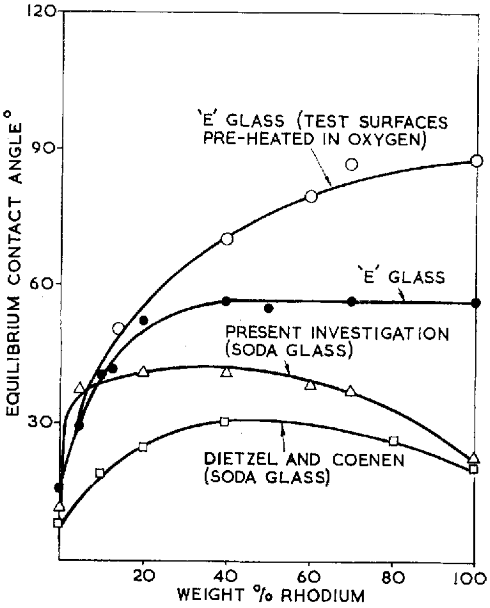

Fig. 3 Contact angles assumed by droplets of soda glass and "E" glass on rhodium-platinum alloys. Alloys having a high rhodium content oxidise when heated in air and this increases considerably the equilibrium contact angle

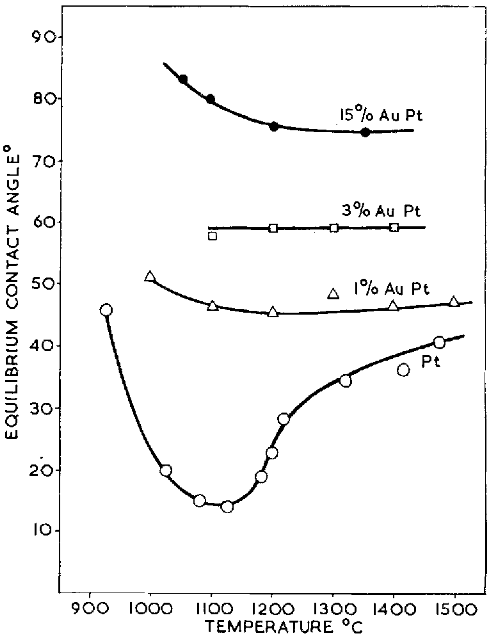

Fig. 4 Effect of temperature on the equilibrium contact angle of "E" glass on gold-platinum alloys heated in air. The addition of even 1 per cent of gold to platinum increases considerably the contact angle assumed by borosilicate glass

resistance to wetting by glass over the entire range of temperature, differences are only significant below 1200°C.

Dietzel and Coenen's results are compared to our own in Fig. 3 which shows the discrepancies observed even when tests were made with a soda glass identical in composition (67 per cent SiO_2, 25 per cent Na_2O and 8 per cent CaO) to that used by these earlier investigators. Although the general trends of the curves were similar, our results indicated a consistently higher contact angle. This effect was found to be due to oxidation. The upper curves in Fig. 3 illustrate how the equilibrium contact angle can be increased by soaking the test specimens in oxygen at 1100°C for 24 hours. The increase in contact angle obtainable by soaking increased with rhodium content, and when a bead of the soda glass referred to above was heated on a freshly polished rhodium surface at 1030°C, a contact angle of 20° was rapidly assumed. The same glass heated on a rhodium surface which had been previously annealed for two hours in air at 1030°C assumed a contact angle of 43°.

Specimen pre-treatment above 1100°C had no effect upon contact angle due, presumably,

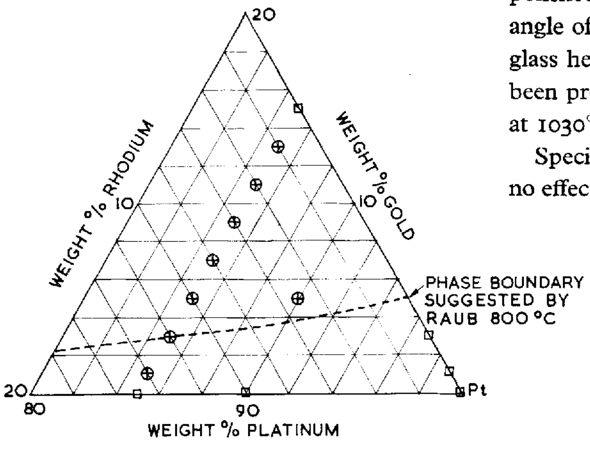

Fig. 5 Diagram showing the compositions of the gold-rhodium-platinum alloys studied in relation to the position of the phase boundary at 800°C suggested by Raub

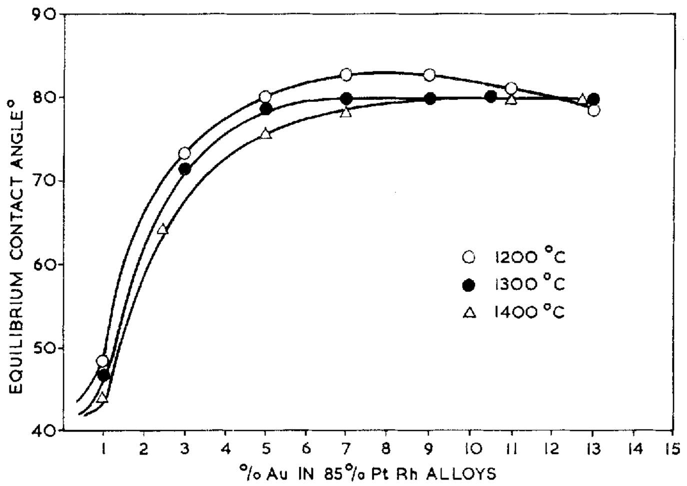

Fig. 6 Effect of gold on the equilibrium contact angle of "E" glass on ternary alloys containing 85 per cent of platinum

to the instability of solid rhodium oxide at this temperature.

Gold-Platinum Alloys

The way in which small additions of gold rapidly increase the resistance to wetting of platinum by borosilicate glass is illustrated in Fig. 4. The equilibrium contact angle of all the gold alloys tested remained remarkably constant with temperature. Three per cent of gold increased the contact angle at 1100°C from 14° to 58° and these promising results encouraged the study of ternary alloys likely to have improved high temperature strength.

Gold-Rhodium-Platinum Alloys

The compositions of the ternary alloys studied in this series of tests are given in Fig. 5. Spectrographic analysis disclosed that the alloys had a total impurity content of approximately 500 ppm, most of which was accounted for by palladium and iridium. Iron and copper represented most of the base metal impurities present.

The effect of gold on the equilibrium contact angle of alloys containing 85 per cent of platinum is shown in Fig. 6. The angle increases rapidly with gold contents up to 5 per cent, but further additions have little effect. The close grouping of the three curves in this figure illustrates the constancy of contact angle of these alloys between 1200° and 1400°C. Similar effects are indicated in Fig. 7, where the equilibrium contact angles assumed by beads of "E" borosilicate glass heated on three different ternary alloys are plotted as a function of temperature. No change in contact angle with time was

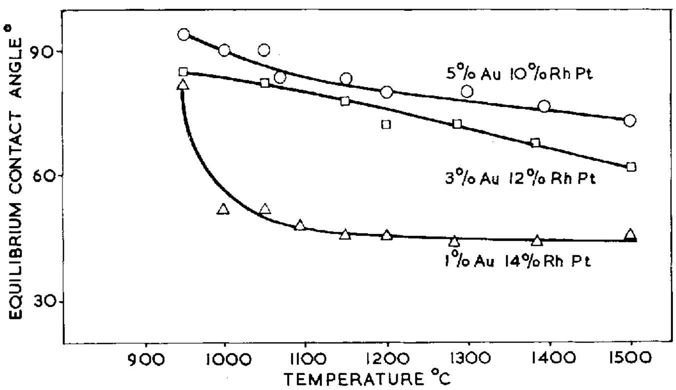

Fig. 7 Effect of temperature on the equilibrium contact angle of "E" glass melted on some representative ternary alloys. The temperature dependence decreases rapidly with increasing gold content. With 5 per cent of gold present the contact angle still exceeds 70° at 1500°C

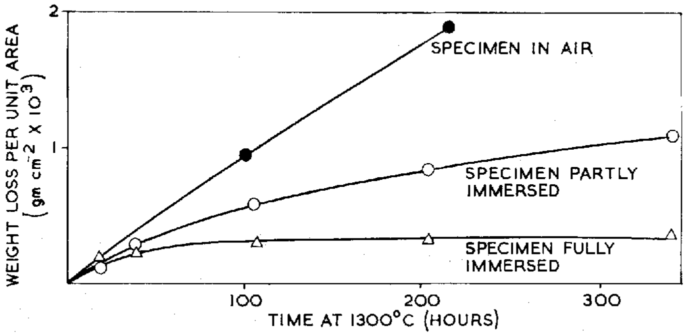

Fig. 9 Curves showing the loss of weight of test plates of the 5 per cent gold-10 per cent rhodium-85 per cent platinum alloy fully and partly immersed in molten "E" glass at 1300°C. Specimens immersed in glass decreased in weight less rapidly than those hung in air at the same temperature

detected on any of the gold-bearing alloys tested.

Because of the high contact angles involved, the beads of glass melted on gold-rhodium-platinum alloys were lightly adherent. Micro-

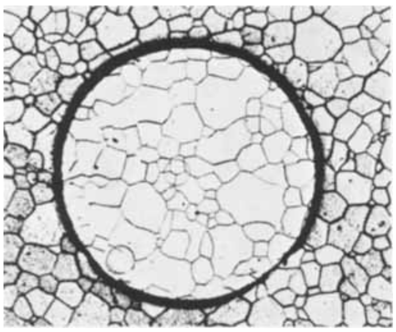

Fig. 8 Plan view of the etched surface left behind after removal of a glass bead from a 5 per cent gold-10 per cent rhodium-platinum test piece (× 30)

examination of the metal surface uncovered by removal of the bead showed a pitting effect similar to that illustrated in Fig. 8. This behaviour suggested solution of the gold-bearing alloy by the glass and led to some loss of weight tests, which were made on flat sheet specimens. These were completely and partly immersed in a bath of "E" glass heated in air at 1300°C for long periods.

Some of the results obtained from these tests are plotted in Fig. 9, which shows that specimens completely immersed in the glass lost less than 0.5 mg of weight per square cm after 340 hours at temperature. The partly immersed specimens lost approximately twice this quantity, and control specimens suspended in air at 1300°C lost weight even more rapidly. These results confirmed that these alloys were attacked more readily by air than by molten glass which did, in fact, exercise a protective effect.

Thermal Hysteresis

An outstanding feature of the test results obtained on the gold-bearing alloys was the

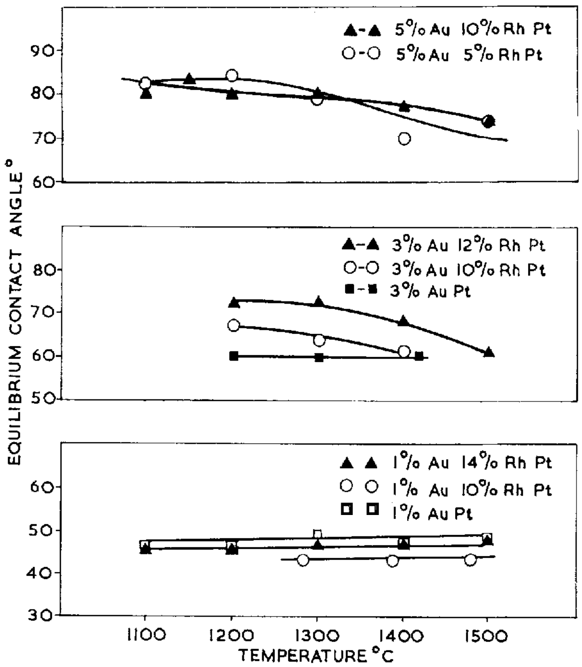

Fig. 10 The equilibrium contact angles of "E" glass on a number of gold- and gold-rhodium-platinum alloys heated in air. The controlling factor is the gold content, and the curves show that temperature and rhodium content have little effect upon the contact angles assumed

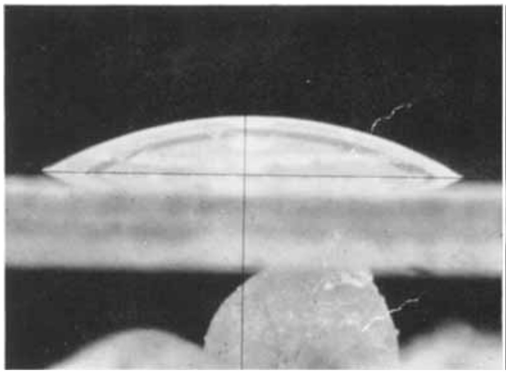

Fig. 11 Droplet of "E" glass in equilibrium with the surface of a 10 per cent rhodium-platinum alloy heated in air at 1200°C (×20)

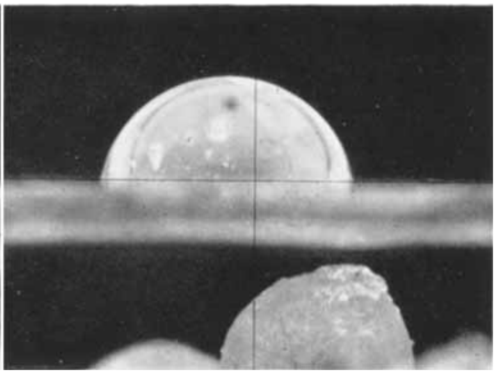

Fig. 12 The high contact angle assumed by a droplet of "E" glass melted in air at 1200°C on the surface of a 10 per cent rhodium-platinum alloy containing 5 per cent of gold (×20)

complete absence of those hysteresis effects characteristic of the behaviour of borosilicate glass on pure platinum. This was undoubtedly due to the fact that in no instance was a minimum detected in the contact angle versus temperature curve. The 10 per cent rhodium-platinum alloy exhibited a slight minimum, and this reflected itself in slight thermal hysteresis. In all the ternary alloys, however, differences between the initially determined contact angle curves and those obtained after thermal cycling were of no practical significance.

Conclusions

The resistance to wetting by molten glass of gold-rhodium-platinum alloys appears to be controlled almost entirely by the gold content. This effect is well illustrated by Fig. 10, which shows that contact angles of 80° at 1300°C are attainable by adding 5 per cent of gold either to pure platinum or to the 10 per cent rhodium-platinum alloy. Figs. 11 and 12 show the completely different appearance of glass beads melted on gold-free and gold-bearing alloys and it seems reasonable to assume that the increased contact angle will result in improved industrial glass handling characteristics.

It is tempting to explain the increased resistance to wetting of the gold-bearing alloys in terms of the unstable nature of the chemisorbed oxygen layer on these materials. Magnetic studies on gold-platinum alloys (5) have shown that unpaired d-band vacancies, known to promote chemisorption are rapidly filled as the gold content increases and this interpretation agrees with the marginal effect of rhodium upon contact angle.

The constitution and high temperature strength of the alloys are now being investigated. At 1400°C the alloy containing 5 per cent of gold, 10 per cent of rhodium and 85 per cent of platinum has been found to be appreciably stronger and more resistant to creep than the binary 10 per cent rhodium alloy. The full results will be reported in Part III of this paper.

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