

# Platinum and the Refractory Oxides

## III — CONSTITUTIONAL RELATIONSHIPS IN THE ALLOYS FORMED

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*Platinum reacts exothermically with aluminium, zirconium and thorium, but is very reluctant to alloy with magnesium. It dissolves 2.2 per cent by weight of aluminium at 1500°C and 10 per cent by weight of zirconium at 1650°C. These wide solid solutions are in equilibrium with very stable intermetallic compounds, thus accounting for the severe reactions which can occur when platinum is heated in contact with alumina and zirconia. Zirconium reacts peritectically with platinum. The effects of these refractory decomposition processes on the long-term stability of platinum thermocouples will be discussed in the fourth and concluding article in this series.*

The extent to which reactions occur when platinum is heated in contact with the more refractory oxides depends very largely upon the affinity of platinum for the metal released by the refractory. Qualitative indications of the dominance of this effect are provided by the extreme reluctance of magnesia to dissociate in the presence of platinum (1). The position of the phase boundaries in the alloys which are formed provides a rather more reliable index of the activity of the dissolved metal. Data obtained in this way, although not particularly accurate, assist in the rational interpretation of experimental findings, and in our attempts to understand the general principles of refractory decomposition constitutional relationships in the alloys of

platinum with aluminium, zirconium, magnesium and thorium have been carefully examined. In the course of this work the solubilities of aluminium and zirconium in platinum have been accurately established for the first time.

### Aluminium-Platinum Alloys

The presently accepted diagram for this system is based on the work of Huch and Klemm (2) who concluded that the first compound to form when aluminium is added to platinum is  $Pt_3Al$  which reacts with the primary solid solution to form a eutectic melting at 1507°C. The compound itself melted at 1556°C and Huch and Klemm were concerned largely with the identification of intermetallic phases and the establishment of solidus and liquidus temperatures. Edshammar (3) commented on the rapid and exothermic reaction which occurred when platinum and aluminium were melted together on a water-cooled copper hearth, although the heats of formation have been determined only in the palladium-aluminium system (4).

As part of our compatibility work the phase boundary of the platinum-rich primary solid solution has been accurately established in these laboratories. Arc melted ingots, prepared from "Thermo-pure" platinum and "Spec-pure" aluminium were homogenised for six hours at 1450°C in vacuum, rapidly quenched and then analysed by chemical methods. The hardness and microstructures of these alloys are given in Table I.

The alloy containing 3.18 per cent of aluminium appeared to be close to the eutectic

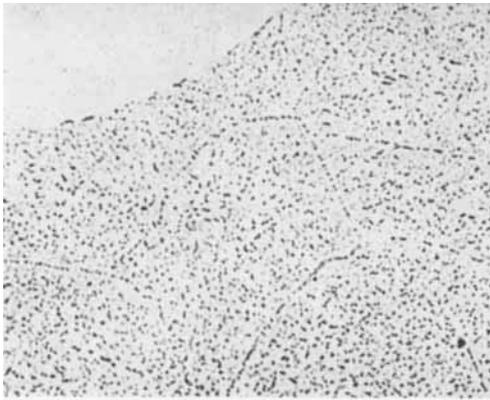


Fig. 1 Alloy containing 2.16 per cent aluminium quenched after 6 hours at 1450°C.  $\times 300$

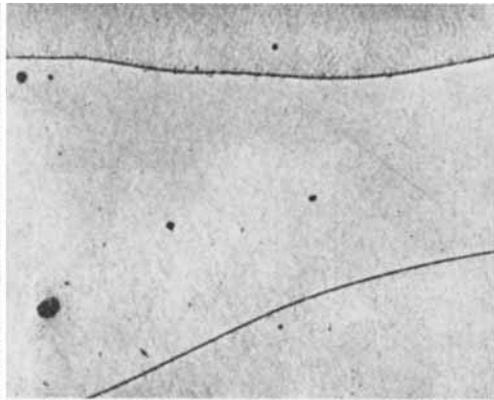


Fig. 2 Alloy containing 2.16 per cent aluminium quenched after a further 3 hours at 1470°C.  $\times 300$

composition. At 1450°C the 2.16 per cent aluminium alloy had a finely dispersed precipitate which dissolved completely when heated to 1470°C, as shown in Figs 1 and 2. Although metallography of this sort helped

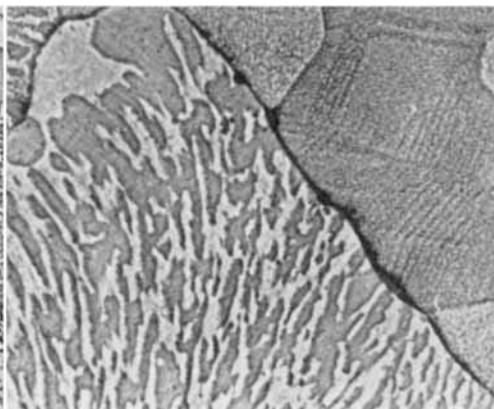
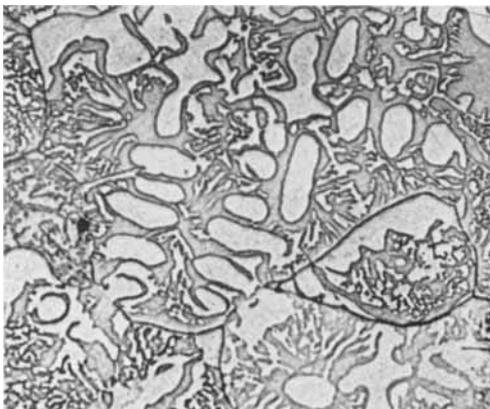
to establish the solubility boundary, most of this information was derived from the electron probe micro-analysis of duplex alloys quenched over a wide range of temperature.

Metallographic methods were, however, used for solidus determinations and it was found that very small quantities of quenched liquid could be detected. Fig. 3 shows the duplex structure of the 3.18 per cent aluminium alloy quenched from 1470°C. Liquid was first detected in this alloy at 1510°C as shown in Fig. 4. This eutectic temperature agrees well with the 1507°C quoted by Huch and Klemm (2). The revised diagram based on metallographic observations and electron probe microanalysis is shown in Fig. 5.

Table I			
Aluminium Content in Wt.% Nominal Analysed		H <sub>v</sub> 100 gm	Structure
0.5	0.52	124	Single phase
1.0	1.06	148	Single phase
2.0	2.16	320	Fine precipitate
3.4	3.18	433	Coarse duplex
4.0	4.18	464	Coarse duplex

Fig. 3 Structure of the 3.18 per cent aluminium-platinum alloy quenched from 1470°C.  $\times 300$

Fig. 4 Quenched liquid round the grain boundaries of the 3.18 per cent aluminium-platinum alloy quenched from 1510°C.  $\times 1000$



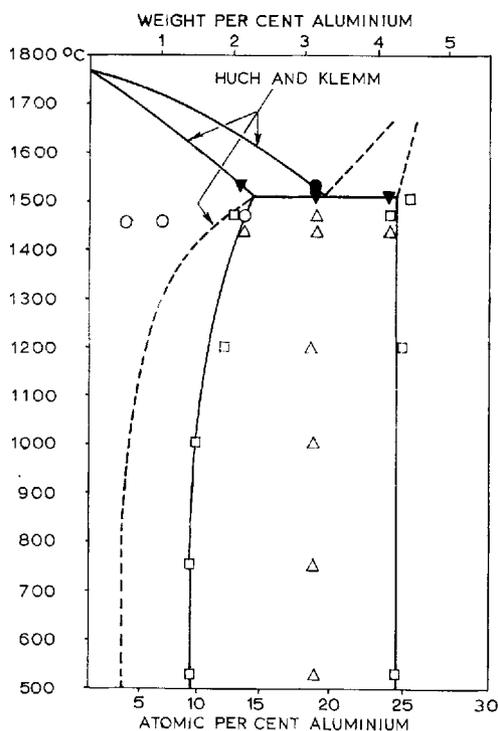


Fig. 5 Platinum-rich end of the aluminium-platinum diagram based on the present work.

○ Single phase alloys    △ Two phase alloys  
 ▼ Incipient melting    ● Complete liquid  
 □ Electron probe microanalysis of two phase alloys

Some lattice parameter measurements obtained on alloys quenched from 1450°C are given in Table II. Powder obtained by filing quenched ingots was stress relieved for six minutes at 800°C for this X-ray examination.

Alloy composition Wt.% Al	Lattice parameter Å	Lattice type
0.52	3.9177	F.C.C.
1.06	3.9124	F.C.C.
3.18	3.9073	F.C.C.
	3.8816	Primitive cubic
4.18	3.917	F.C.C.
	3.879	Primitive cubic
Pure Pt	3.9231	F.C.C.

Aluminium reduces the lattice spacing of platinum from 3.9231Å to 3.9124Å when 1 per cent by weight has been taken into solution. The compound Pt<sub>3</sub>Al which separates out at higher concentrations has a primitive cubic structure of the Cu<sub>3</sub>Au type. Our value of 3.879Å for the spacing of this phase agrees reasonably well with the 3.876Å quoted by Klemm, although our values for the parameters of the platinum-rich solid solution in this two-phase region are somewhat anomalous. These variations may perhaps be associated with the presence of an ordered phase, first mentioned by Bronger and Klemm (5), who suggested its formation at temperatures below 1300°C in the duplex region by reaction between Pt<sub>3</sub>Al and the primary solid solution. Confirmatory work is obviously required in this region.

### Zirconium-Platinum Alloys

The zirconium-platinum diagram, based on the work of Kendall, Hays and Swift (6), shows that the solubility of zirconium in platinum is less than 1 per cent by weight although little metallography was carried out in this region. The compound Pt<sub>3</sub>Zr had a melting point in excess of 2120°C and Raman and Schubert (7) concluded that it had a hexagonal TiNi<sub>3</sub> structure with  $a = 5.624\text{Å}$  and  $c = 9.213\text{Å}$ .

The zirconium solubility values were obviously in error, however, as it was known that platinum containing up to at least 2 per cent by weight of zirconium has a single phase structure and can be readily rolled and drawn into wire. In order to establish the true solubility of zirconium in platinum, alloys containing up to 14 per cent by weight of zirconium were made up in the arc furnace from "Thermo-pure" platinum and "Spec-pure" zirconium rods, the latter having a total impurity content less than 0.01 per cent. Considerable heat was evolved when these metals began to run into each other under the arc. Table III indicates the composition, microstructure and hardness of these alloys after homogenisation for 16 hours at 1650°C in vacuum followed by quenching in silicone oil.

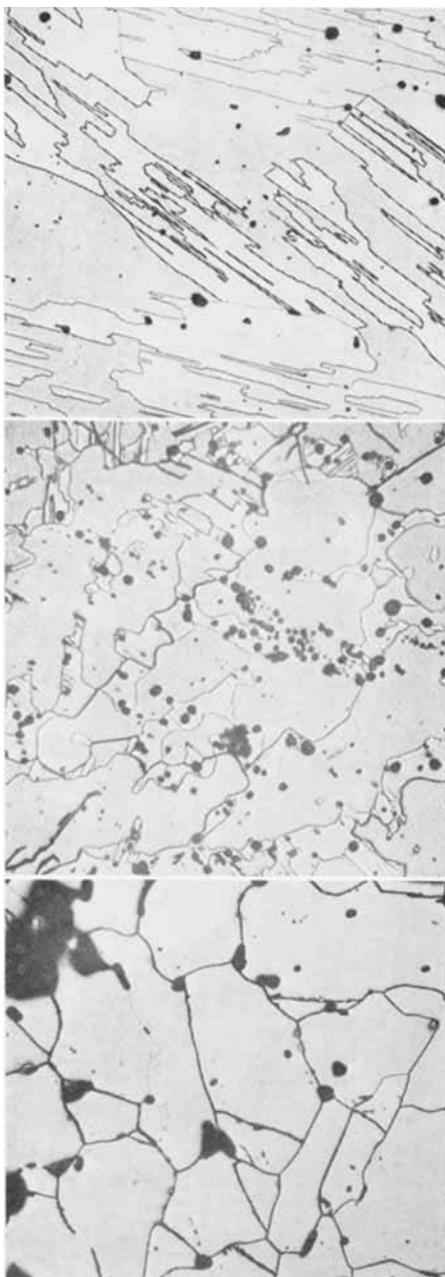


Fig. 6 Heavily twinned microstructure of solid solution platinum alloy containing 9.77 per cent by weight of zirconium quenched from 1650°C.  $\times 300$

Fig. 7 Duplex alloy containing 12.00 per cent by weight of zirconium after quenching from 1650°C.  $\times 300$

Fig. 8 Platinum alloy containing 13.5 per cent by weight of zirconium after quenching from 1650°C. This alloy consists almost entirely of the compound  $Pt_3Zr$ .  $\times 300$

The 12 per cent zirconium alloy, after quenching from 1650°C contained two well defined phases, the general appearance of which was more reminiscent of a peritectic than a eutectic microstructure. The metallographic work demonstrated quite conclusively the extremely narrow range of the duplex region between the platinum-rich primary solid solution and the compound  $Pt_3Zr$ . Fig. 6 illustrates the heavily twinned solid solution alloy containing 9.77 per cent by weight of zirconium after quenching from 1650°C. The 12 per cent zirconium alloy shown in Fig. 7 contains 20 to 30 per cent by volume of the zirconium-platinum intermetallic, while the alloy containing 13.5 per cent of zirconium shown in Fig. 8 consists almost entirely of the compound  $Pt_3Zr$ . The platinum-rich solid solution in this alloy could just be detected by X-ray methods. The lattice parameter measurements for the hexagonal structure agree with those of Wallbaum (8) but not Schubert (7).

Several solidus determinations were made on alloys heated *in vacuo* in a tantalum resistance furnace. The specimens were suspended on tungsten-rhenium wires and quenched in silicone oil. Micro examination of these quenched specimens showed that the platinum-rich end of the diagram was of the peritectic type rather than a eutectic as had been hitherto suggested.

The present experimental results, supplemented by Kendall's (6) melting point determinations, have been plotted on Fig. 9 which provides a self-consistent interpretation of the data available. Further work is obviously required to establish the true shape of the solubility curve at lower temperatures and to ascertain over what range of compositions the  $Pt_3Zr$  phase exists.

### Thorium-Platinum

The diagram advanced by Thomson (9) shows the formation of a eutectic between  $Pt_5Th$  and platinum at a temperature of  $1337 \pm 12^\circ C$ . The solubility of thorium in platinum was not determined.

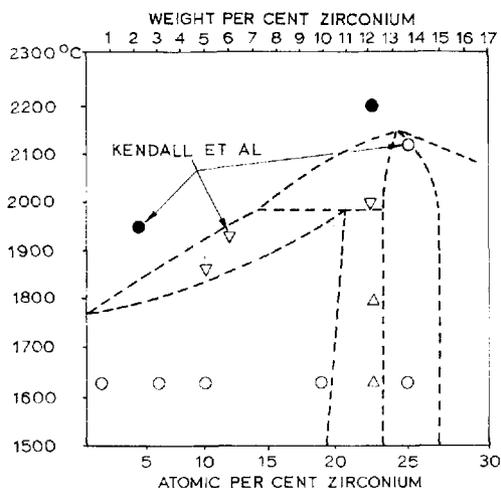


Fig. 9. Revised diagram for the platinum-rich end of the zirconium-platinum system.

- single phase alloys      △ Two phase alloys
- ▽ liquid and solid        ● Complete liquid

In view of the very deleterious effects which thoria can have upon platinum, the microstructure and composition of the alloys formed has received considerable attention. No evidence of thorium solubility in the primary crystals has been detected with the electron probe micro-analyser although this cannot be regarded as conclusive evidence since the limit of detection of thorium in platinum by this technique is found to be approximately 0.2 per cent by weight.

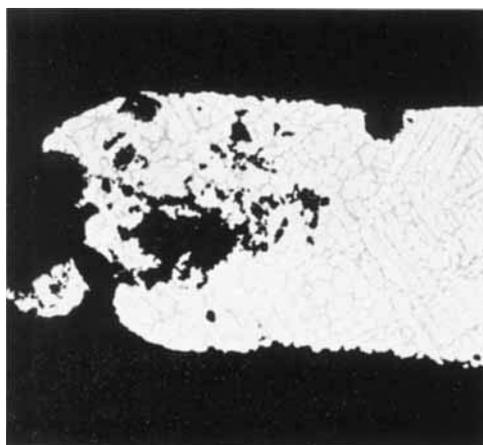


Fig. 10 Microstructure of platinum which fused completely after contact with thoria for 1 hour at 1700°C in pure argon. × 150

Very severe reactions occurred, however, when platinum was heated in contact with thoria under a pure argon atmosphere. Fig. 10 illustrates the microstructure of a specimen which fused completely after three hours at 1700°C under these conditions.

The melting point of Pt<sub>5</sub>Th, suggested as being somewhat higher than 1500°C (9) does not in itself indicate an extremely high stability. High heats of formation are obviously associated with the exothermic reactions which occur wherever thorium and platinum are melted together. The high mutual affinity of the two metals reflects itself

Analysed composition % by weight of Zr	Hardness H <sub>v</sub> 100g	Microstructure	Phase	Lattice parameters
0.87	152	Single phase	F.C.C.	
1.04				
3.05	398	„	F.C.C.	3.955Å
4.97	455	„	F.C.C.	3.968Å
9.77	844	„	F.C.C.	
12.00	845	(Heavily twinned) Duplex	F.C.C.	
13.50	846	Almost completely single phase	H.C.P. H.C.P.	a=5.664Å c=9.255Å

therefore in the ability of platinum to accelerate the decomposition of thorium.

The reactions which occur must, however, be carefully distinguished from these between aluminium and zirconium with platinum. In the absence of detectable solubility any elementary thorium which contacts platinum above  $1337^{\circ}\text{C}$  will immediately form liquid. Diffusion in the liquid state is rapid, so that thin liquid eutectic films on the platinum surface could expedite the transfer of thorium from the surface of the platinum to its interior. The only essential requirement for such a reaction is a stable liquid phase capable of retaining dissolved thorium in a state of low activity.

### Magnesium-Platinum

Bronger and Klemm (5) were able to produce magnesium-platinum alloys by reducing magnesia in contact with platinum with carefully dried ammonia. The reductions proceeded further and more completely at  $1100^{\circ}\text{C}$  than at  $1200$  to  $1400^{\circ}\text{C}$  and at these lower temperatures platinum solid solutions containing up to 28 atomic per cent of magnesium were obtained. Two ordered phases, based on the compositions  $\text{Pt}_7\text{Mg}$  and  $\text{Pt}_3\text{Mg}$  were detected within this solid solution field.

Magnesium-platinum alloys are not readily obtained by conventional melting methods. Large quantities of magnesium are lost by evaporation and exothermic reactions such as those between aluminium and platinum do not occur. Even by their direct reduction method Bronger and Klemm were unable to produce magnesium-rich alloys and we must conclude that platinum and magnesium alloy with extreme reluctance.

Fig. 11 illustrates the microstructure of a platinum alloy containing approximately 1.5 per cent by weight of magnesium. This alloy was made by argon arc melting, and of the 3 per cent of magnesium added only half remained. To avoid loss of magnesium during homogenisation the ingot was packed in magnesia powder and sealed up in an

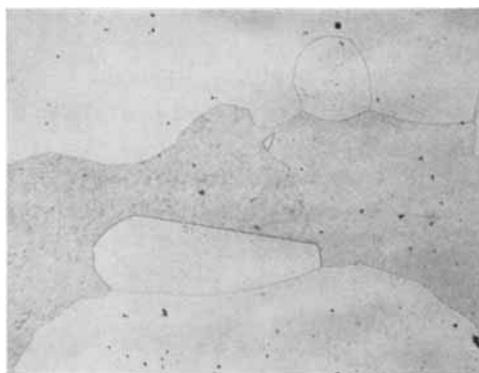


Fig. 11 Microstructure of platinum containing 1.5 per cent by weight of magnesium after homogenisation for 16 hours at  $1400^{\circ}\text{C}$  followed by quenching.  $\times 75$

evacuated platinum tube by pressure welding. After soaking for 16 hours at  $1400^{\circ}\text{C}$  the capsule was quenched into water, its composition being then checked by micro-probe analysis. No compound was detected in this alloy, which contains 11 atomic per cent of magnesium and falls just within the region of possible ordering described by Bronger and Klemm (5). As quenched from  $1400^{\circ}\text{C}$  this alloy had a hardness of  $225\text{H}_v$  (25g).

### Conclusions

Platinum reacts exothermically with aluminium, zirconium and thorium, and this tendency towards compound formation provides the driving force for the refractory decomposition processes which can occur at high temperatures. The affinity of platinum for magnesium is low and magnesia shows, therefore, little tendency to decompose on heated platinum surfaces.

The solubility of aluminium in platinum is much higher than had hitherto been supposed and the ability of solid platinum to dissolve 10 per cent by weight of zirconium is particularly noteworthy. When saturated, this solid solution is in equilibrium with the compound  $\text{Pt}_3\text{Zr}$ . At lower concentrations the dissolved metal is held in a state of activity even lower than that which exists in the compound. As evidenced by the decomposition processes which have been observed, the

affinity for zirconium of very dilute zirconium-platinum alloys appears to be very formidable indeed.

Although thorium is almost completely insoluble in solid platinum, the heat that is evolved when liquid alloys are formed confirms the very high affinity of platinum for thorium. In the absence of terminal solid solubility any thorium vapour which meets a platinum surface at temperatures above 1337°C will immediately form liquid. The presence of such a liquid layer on a solid platinum surface would be expected to facilitate metal transfer processes.

The practical implications of these refractory decomposition processes for the long-term stability of platinum thermocouples when in contact with various refractories will be discussed in the final article in this series.

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# Combined Catalysts for Ammonia Oxidation

## PLATINUM ALLOY GAUZZES IN NITRIC ACID PRODUCTION

Oxidation of ammonia over platinum alloy gauzes remains the most efficient method of producing oxides of nitrogen in nitric acid plants. However, studies in Russia have been directed towards replacing part of the pad of platinum alloy gauzes used in the conventional reactor by non-platinum metal catalysts. As long ago as 1958 Russian workers showed that combined catalysts, consisting partly of gauzes and partly of a layer of another catalyst, were effective in ammonia oxidation, thereby reducing both the amount of platinum alloy gauze required and the loss of platinum metal from the gauze during the reaction.

A. P. Zazorin, N. F. Kleshchev and V. I. Atroshchenko have now shown (*Khim. Promyshlennost'*, 1970, (7), 513-514) that a layer of iron oxide-chromium oxide catalyst can be used in conjunction with platinum alloy gauzes in high pressure ammonia oxidation plants. Most of the conversion still takes place on the platinum alloy gauze and the total yield of the combined catalysts is somewhat less than where gauzes alone are used but if economic considerations dictate the use of less platinum than the studied method is a practical proposition.

Tests were carried out at pressures of 5 and 10 atmospheres and at 1150 K using a pad of seven palladium-rhodium-platinum gauzes and a layer of 93 per cent  $\text{Fe}_2\text{O}_3$  - 7 per cent  $\text{Cr}_2\text{O}_3$  catalyst of thickness varying from 120 to 270 mm. The amount of ammonia conversion at the platinum alloy gauze was 81 per cent at 5 atm, and 78 per cent at 10 atm. As the layer of iron-chromium oxide increased in thickness the total conversion rose from 91 to 97 per cent at 5 atm, and from 87 to 94.5 per cent at 10 atm, i.e., a greater thickness of the non-platinum metal catalyst bed results in greater conversion, as might have been expected.

The authors suggest that a layer of oxide catalyst 25 to 30 mm thick is equivalent to one platinum gauze, a layer 120 mm thick to 4 to 5 gauzes; 270 mm thick, 9 to 11 gauzes.

The normal practice of the authors appears to have been to use a pad of from 16 to 19 gauzes at these pressures. They now suggest that a pad of 6 to 7 gauzes with a catalyst bed 200 to 220 mm thick is adequate at 5 atm, and that a bed of oxide catalyst 300 to 330 mm thick is adequate with the same number of gauzes at 10 atm.