

Fig. 2 Fused zone of platinum thermocouple limb after failure in contact with fine "Purox" alumina powder after 8½ hours at 1475°C under a gettered argon atmosphere. ×150

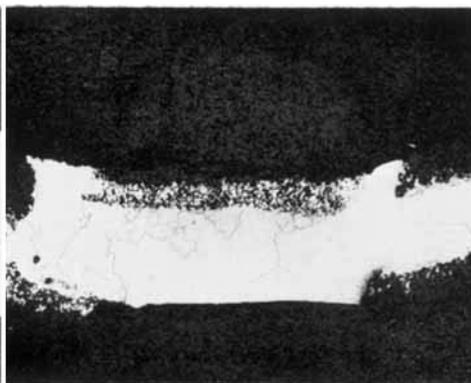


Fig. 3 Fused zone of platinum thermocouple limb after failure in contact with coarse "Purox" alumina powder after 65 hours at 1475°C under a gettered argon atmosphere. ×125

surface areas of the two reactants and also the volume of the voids between them.

By increasing the diameter of the refractory particle we arrive eventually at the stage when a small particle of platinum contacts a refractory surface of such a large radius that it can be considered a plate. A further change in curvature of this refractory surface results in partial encapsulation of the platinum. One practical exemplification of this configuration is the containment of platinum in a crucible. A limiting stage in the changing curvature of the refractory is arrived at when the platinum is completely surrounded on all sides with oxide.

After the curvature of the platinum particle is changed through the same sequences we arrive eventually with a particle of refractory oxide completely surrounded with platinum. Platinum cermets form a good illustration of this important configuration.

Effect of Oxide Particle Size

The effect of varying the particle size of the refractory relative to that of platinum was studied in the test cell using "Purox" alumina. Tubular alumina insulators were crushed and sieved to provide "fine" (less than 200 mesh) and "coarse" (16 to 60 mesh) powders of identical composition, and the uncrushed "Purox" tubes provided a reason-

able approximation to the geometry where point contact exists between platinum and a relatively flat refractory surface.

The tests in the fine and coarse grades of crushed alumina powder under gettered argon were cut short by fusion of the platinum limbs after, respectively, 8½ and 65 hours at 1475°C. The microstructures of the fused zones are illustrated in Figs 2 and 3. Reactions in the coarse oxide bed were confined to areas of direct physical contact between the platinum and the oxide particles. This effect was particularly noticeable in the alloy limb where the rhodium addition appeared to restrict the solid state diffusion of aluminium into platinum. Generally speaking, inter-reactions between the thermocouple limbs and the coarse refractory oxide appeared to be most severe in regions close to the surface of the bed, although failure occurred close to the hot junction.

In the fine oxide powder bed, failure occurred immediately below the surface in the gettered argon atmosphere. Metallographic examination revealed extensive contamination throughout the thermocouple limbs with the surprising exception of the rhodium platinum limb in those areas close to the oxide surface. Corresponding areas on the platinum limb had suffered severely.

Under vacuum conditions the thermo-



Fig. 4 Local areas of reaction between pure platinum and the coarse alumina particles in contact with it after 72 hours at 1475°C in vacuum. $\times 150$

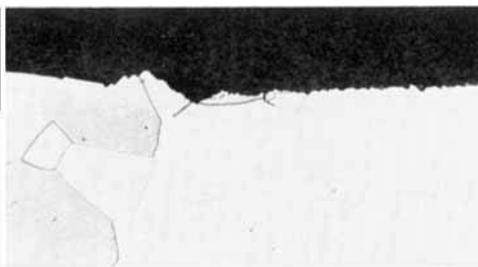


Fig. 5 Local reaction area in 13% rhodium-platinum wire due to point contact with "Purox" alumina thermocouple tube in a gettered argon atmosphere for 180 hours at 1475°C. $\times 150$

couple heated in the coarse grade of alumina powder survived for 72 hours at 1475°C without failure. In this instance, reaction was not confined to those portions of the wire close to the surface of the refractory bed, substantial quantities of aluminium being detected throughout the immersed length of the thermocouple. The reaction was limited, however, to those points along the wire surface which were in direct contact with alumina particles as illustrated in Fig. 4.

The thermocouple heated within a single alumina insulator under the gettered argon atmosphere maintained its thermoelectric output, within the limits of experimental error for the 180-hour test period. In contrast, the corresponding thermocouple heated in vacuum exhibited a large drop in output at the gold point after 140 hours at temperature. Microexamination and analysis of the wires indicated that in both instances the alumina had reacted with the thermocouple limbs at the ends of the tubing where extremely local contact had been made.

Under the argon atmosphere, visible evidence of reaction was detected in the form of a second phase at the surface of the rhodium bearing leg as shown in Fig. 5. Aluminium had diffused away to broaden the affected area during the run, and was detected at distances up to 800 microns away from the main seat of the reaction, which coincided with the point of contact between the inner edge of the tube and the wire emerging from it. The platinum leg had been similarly,

although a little more extensively, affected at the point where it emerged from the opposite end of the insulator.

Traces of aluminium were also detected in the limbs close to the hot junction enclosed within the tube after heating in gettered argon, although this did not occur after vacuum testing, when the reaction zones were more limited in extent and confined entirely to the points of contact at the extremities of the insulator. Rhodium evaporated rapidly from the alloy limb in vacuum, and this probably accounted for the deterioration in thermal EMF.

Thermocouples in vacuum furnaces operate under conditions very similar to those arranged in this experiment. Their deterioration in electrical performance can be directly attributed to rhodium evaporation, and the reactions with the alumina insulators are fairly local and not serious enough to cause premature mechanical failure unless the thermocouple is severely disturbed.

This series of tests showed that the rate and extent of contamination increases with the surface area of the refractory oxide. Extremely rapid failure occurred when the platinum wires were heated in fine alumina powders, whereas reaction with a rigid smooth alumina tube of low surface area was largely confined to points of local contact. The profound effect of surface area upon the rate of reaction implies the operation of vapour phase transfer processes which will be discussed at a later stage in this article.

Vacuum Melting Experiments

The containment of molten platinum within a refractory crucible exemplifies one of the more important configurations symbolised in Fig. 1 and it is of interest therefore to consider the extent of the contamination introduced into induction-melted platinum by metal/crucible reactions.

The following results were obtained when a 200 ounce charge of platinum sponge was induction melted in a calcium-stabilised zirconia crucible, which was 2.75 inch bore and 5.5 inch high. The sponge was introduced into the crucible in the form of pressed bars and melted initially for 5 minutes in air to remove volatile salts and other non-metallic impurities. The furnace was then evacuated, over a further period of 5 minutes to a pressure of about 2×10^{-4} Torr and the molten charge held at this pressure, at about 1850°C , for a total period of 105 minutes.

The following analytical information was obtained from dip samples taken from the melt at 15-minute intervals during this period:

Dip sample	Zirconium content %
1	0.021
2	0.056
3	0.065
4	0.092
5	0.104
6	0.116
7	0.129

The above results were obtained using a crucible in which several previous platinum melts had been made. The tendency for contamination to increase with the number of melts appeared to be associated with a leaching action which roughened the interior surface of the crucible during vacuum melting and increased the area of the refractory/molten platinum interface. In general, the zirconium reversion occurred less rapidly when new crucibles were used, and melts held for up to 15 minutes in these crucibles under vacuum conditions were rarely contaminated to an unacceptable degree.

Surface area appears again, therefore, to be an important factor in platinum/refractory reactions, although the extent of the contamination introduced into the molten platinum was fairly minor compared to that which occurred in the earlier solid state experiments. During vacuum melting, reaction rates must obviously be controlled by conditions at the interface, where the development of small partial pressures of oxygen would hinder any rapid dissociation process. The area of the reaction interface, although increased by the leaching action, is relatively small in relation to the volume of platinum present, and the hydrostatic pressure of the melt would also tend to hinder any reactions which evolved a vapour phase.

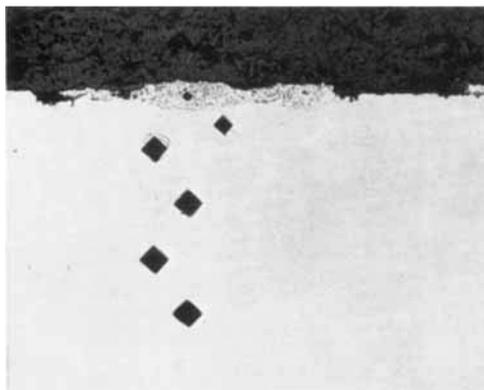


Fig. 6 Interface between platinum and stabilised zirconia coating after 190 hours at 1400°C in carbon monoxide. $\times 250$

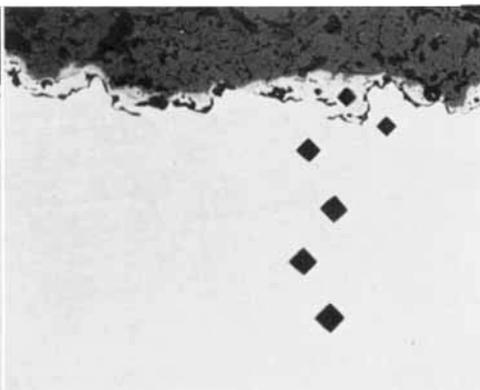


Fig. 7 Interface between platinum and stabilised zirconia coating after 190 hours at 1400°C in vacuum. $\times 250$

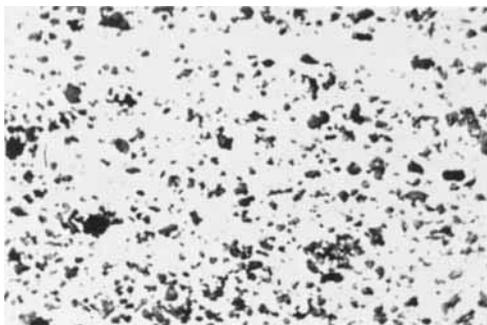


Fig. 8 Zirconia particles in platinum-zirconia cermet after consolidation and hot rolling. $\times 300$

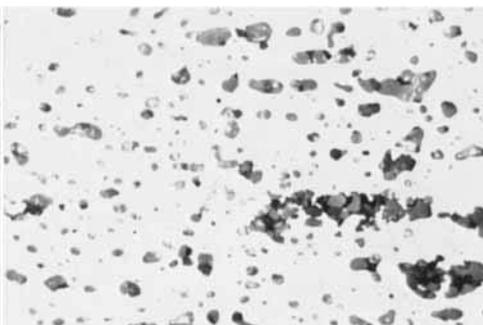


Fig. 9 Zirconia particles in platinum-zirconia cermet after heat treatment for 700 hours at 1400°C. $\times 300$

Vacuum melting presents, therefore, an interesting intermediate stage of a configuration which inhibits but does not completely prevent the escape of volatile reaction products.

Reactions at a Confined Interface

Extreme examples of the configurations symbolised in Fig. 1 occur when platinum becomes completely encapsulated in refractory, or the refractory oxide becomes completely encapsulated in platinum. In both instances the metal released by the dissociation of the refractory can be removed by the platinum. The slightest dissociation will, however, evolve oxygen and the extent to which the reaction can proceed depends upon the rate at which this gas is removed.

Platinum sheet and wire can be encapsulated in zirconia by flame and plasma spraying. The resultant coatings, although strong mechanically and resistant to thermal cycling, are obviously not completely resistant to oxygen permeation. Figs 6 and 7 illustrate the metal/refractory interfaces of such encapsulations after heat treatment for 190 hours at 1400°C. Considerable surface alloying has occurred in the carbon monoxide atmosphere. In vacuum the reaction, although irregular, has penetrated locally well into the platinum rods. These reactions are less severe than those which occur when platinum wires are heated in contact with loose beds of zirconia powder and it must be con-

cluded that the zirconia sheath, though imperfect, retards considerably the removal of free oxygen from the reacting interface.

Complete retardation occurs when the oxide particles are entirely surrounded with platinum. This condition prevails in a platinum-zirconia cermet as shown in Figs 8 and 9. The particles of oxide, after consolidation and hot rolling are fine and well distributed. After heat treatment for nearly 700 hours at 1400°C no evidence of dissociation can be detected. The oxide particles retain their identity although growth of the large particles at the expense of the smaller has occurred in accordance with normal laws.

Temperature Gradients

Strong temperature gradients were an essential feature of the experimental conditions within the glass test cell, and to allow their influence on platinum/refractory reactions to be evaluated, further compatibility trials were made in a resistance heated furnace which ensured that the thermocouple wire and its associated refractory bed was maintained at temperatures uniform to about 10°C.

The thermocouples were immersed to a depth of about 2 inches in fine alumina powder having impurities as listed in the previous article (1). Approximately 50 gm of powder were contained in a "Purox" alumina crucible, and the initial tests at 1500°C were made in an argon atmosphere gettered by the tantalum furnace tube. Under such condi-

tions both limbs of the thermocouple melted completely after only two hours. The fused areas were found to contain, in addition to the normal eutectiferous networks of aluminium-platinum phases, areas of the platinum-platinum silicide eutectic.

The silicon must have come from the alumina powder and from the "Purox" alumina crucible which were the only non-metallic components within the furnace. Although the alumina powder contained only about 5 p.p.m. of silicon, its total weight exceeded that of the thermocouple wire by many times, a situation which did not exist in experiments made in the normal test cell, where the weight of powder actually at the platinum wire temperature was very small. When further experiments were made in this resistance furnace, in argon at 1250°C no evidence of siliceous contamination was observed. The e.m.f. of the thermocouple changed little in spite of the considerable quantities of aluminium detected along its immersed length.

Vacuum experiments were made in the same resistance heated furnace. A molybdenum heater tube was used so that excessive gettering action would be avoided, and the vacuum obtained would be comparable in quality to that used in the standard test cells.

After 72 hours at 1500°C in vacuum it was found that considerable amounts of aluminium had been uniformly alloyed along the whole length of both thermocouple limbs, which however had not melted. This tendency for the whole length of the thermocouple to react with the oxide in vacuum under the uniform temperature conditions prevailing in the resistance furnace was confirmed by further experiments made at 1200°C.

The intense local attack, in vacuum, which occurred in the glass test cells at or near the surface of the refractory bed was therefore a consequence of the temperature gradient present in that region. The finding that the rate and severity of platinum/refractory reactions increased greatly with the weight of refractory powder actually maintained at the

reaction temperature helps to confirm the vapour phase concept of metal transport.

Effect of Temperature

Although the time taken for a thermocouple to fail mechanically does not always reflect the extent to which it has become contaminated, the gradual accumulation of test results showed a surprisingly well-defined relationship between temperature and time to failure with the standard 13 per cent rhodium-platinum thermocouple. The data used to plot the graphs shown in Fig. 10 were obtained in glass test cell experiments when standard thermocouples, 0.020 inch diameter, were immersed in beds of 100 mesh alumina powders.

The shape of the curves is to some extent fortuitous, because the couples take up more aluminium over the longer test period at the lower temperatures. The determining factor is, presumably, the time taken for the couple

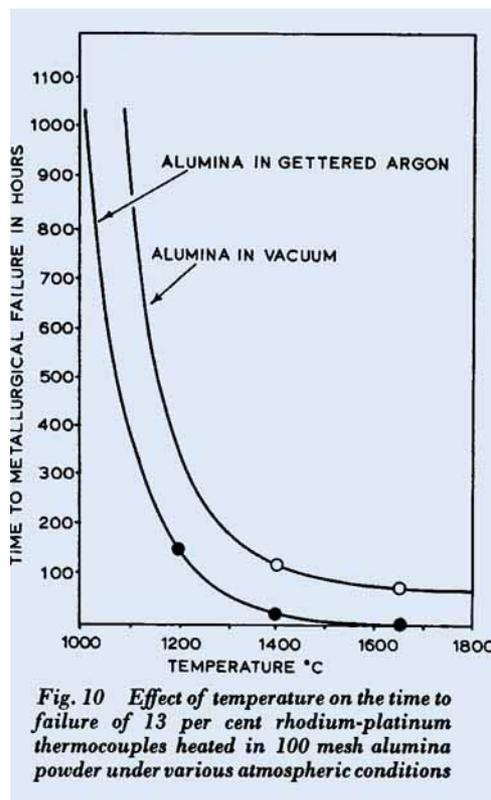


Fig. 10 Effect of temperature on the time to failure of 13 per cent rhodium-platinum thermocouples heated in 100 mesh alumina powder under various atmospheric conditions



Fig. 11 Pt:13 per cent Rh-Pt thermocouple after 113 hours at 1700°C in thoria in vacuum. $\times 2.5$

to absorb sufficient aluminium to cause it to melt at the test temperature. Couple lives, in alumina under a gettered atmosphere, are less than 2 or 3 hours at 1650°C. Under vacuum conditions at this temperature couples last for approximately 80 hours before failure and in argon of commercial purity tests of well over 1000 hours at 1600°C have shown only minor deterioration.

No metallurgical failures in magnesia powders have been obtained even in gettered argon at 1700°C. The changes in thermoelectric output at this temperature are very small.

Discussion

It can be concluded from this work that reactions between platinum and the refractory oxides are controlled by the affinity of platinum for the metal released on decomposition, by the surface area of the reacting substances, and by the rate at which oxygen and metal vapours can be removed from the reaction zone. It is probably safe to suggest that vapour phase transfer accounts for most of the metal transfer observed, as the reactions proceed most rapidly in fine beds of powders where surface areas are high and also in large heated beds of refractory, where higher metal vapour concentrations might be expected to develop.

The main difficulty is to explain why the vacuum reactions are slower and different in character to those which occur in highly pure argon. The vapour phases so far discussed have been those released by the process of decomposition and it is important, therefore, to consider the complicating effects of platinum vapour, which at 1600°C has a saturation pressure of the order of 10^{-5} Torr, one order of magnitude higher than that of the aluminium or oxygen partial pressures.

At 1600°C, platinum evaporates in vacuo at a rate of approximately 10^{-7} gm/cm² sec, while rhodium leaves the heated surface even faster. It seems not unreasonable to suggest, therefore, that thermocouples heated in vacuum are attacked less rapidly by alumina than they are in pure argon simply because the aluminium alloy which develops in inert atmospheres evaporates in vacuum as soon as, or even before, it is formed. Evidence in favour of this hypothesis is provided by the thermoelectric measurements made during the course of these experiments. In all the vacuum test runs, rhodium was lost at a high rate by evaporation, and since this reflected itself in reduced thermal e.m.f.s, a low thermal output generally coincided with the local aluminium attack just below the refractory surface which was a characteristic feature of these low pressure experiments.

How, therefore, do we account for this rapid attack in vacuum below the refractory surface? It is obviously associated with the steep temperature gradient which exists in this region as it does not occur when temperatures are uniform. Variation of temperature affects the rate, but not the position of this local attack which is well illustrated by Fig. 11. In this region, aluminium or any other contaminating metal must be absorbed by the wire faster than platinum can evaporate. This implies a temperature level for the wire in this region which is low relative to the ambient pressure of contaminating metal vapour within the bed of powder.

By plotting the vapour pressure of platinum as a function of temperature on the same

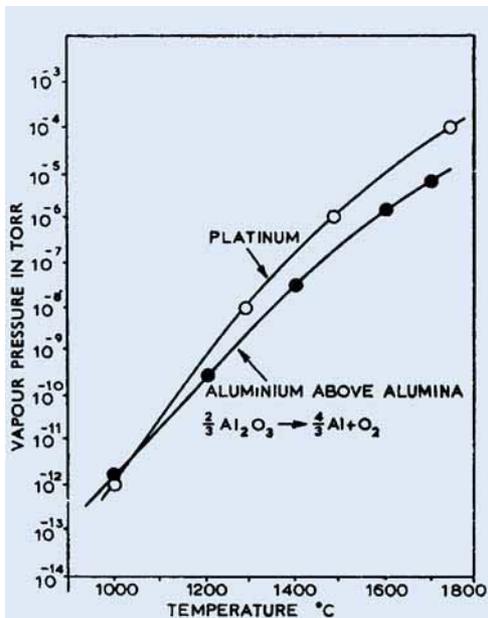


Fig. 12 Saturation vapour pressure curve for pure platinum plotted on the same co-ordinates as the aluminium-alumina dissociation vapour pressure curve

co-ordinates as the aluminium-alumina dissociation vapour pressure curve we obtain two curves of the form shown in Fig. 12. The horizontal temperature interval between the two lines is the minimum which need exist between decomposing alumina and a platinum surface before aluminium will tend to deposit and be absorbed on the latter.

Optical pyrometer measurements indicated that under vacuum conditions the wires entering the refractory bed were approximately 150°C cooler than the temperatures corresponding to the thermal e.m.f. generated by the immersed hot junction. Fairly strong temperature gradients thus existed in the emerging portions of the wires and it became possible to envisage a mechanism whereby attack from the heated alumina particles was confined to fairly small regions of the platinum wire close to the surface of the refractory bed.

The curves shown in Fig. 12 suggest the interesting possibility that at test tempera-

tures below 1000°C the reaction in vacuum atmospheres should proceed at all points along the wire, and further work at these lower temperatures would obviously contribute greatly towards our understanding of these reactions.

The extreme reluctance of magnesia to dissociate at high temperatures shows that the affinity of platinum for the metal released by the refractory is a dominant factor which obviously overrides most of the geometrical and environmental conditions so far considered, since the magnesium-magnesia dissociation pressure is at all temperatures higher than the vapour pressure of platinum. Zirconia and thoria lie at the opposite ends of the scale, the metallic vapour pressures of zirconium and thorium lying well below that of platinum. Whilst explaining the tendency for reactions between these oxides and platinum to occur at positions fairly well removed from the wire surface, vapour pressure considerations do not easily lend themselves to an explanation for all the geometrical effects observed when these oxides were examined in the test cell arrangement.

Constitutional relationships in the alloys of platinum with aluminium, magnesium, zirconium and thorium will be reviewed in subsequent articles, which will also deal with the effects on the user of platinum of the processes leading to this type of reaction.

It is important that reactions of the type described should not be considered merely in their negative aspects as additional obstacles in the already difficult field of high temperature research. The metallurgist might well exploit them for the production of inter-metallic compounds and dilute solid solutions.

Acknowledgements

Acknowledgements are due to the United Kingdom Atomic Energy Authority who supported much of this work. We are particularly indebted to Mr J. P. Evans and Dr L. E. Russell, Process Technology Division at Harwell, for their help and encouragement.

References

- 1 A. S. Darling, G. L. Selman and R. Rushforth, *Platinum Metals Rev.*, 1970, **14**, (2), 54-60