

Platinum and the Refractory Oxides

I – COMPATIBILITY AND DECOMPOSITION PROCESSES AT HIGH TEMPERATURES

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Under normal atmospheric conditions platinum is exceedingly inert with respect to the more refractory oxides. Severe reactions can occur, however, when the oxidising potential of the surrounding atmosphere is reduced below a critical level. Alumina, zirconia and thoria dissociate, oxygen is evolved and platinum extracts the metal from the refractory to form dilute alloys and low melting point phases. Magnesia is very resistant to this type of decomposition, and appears to be an excellent refractory for use in contact with platinum. This article describes in general terms the reactions of platinum with alumina, zirconia, magnesia and thoria at temperatures up to 1700°C. Subsequent articles will discuss the effects of geometry and environment on such reactions, and finally their practical implications so far as the user of platinum is concerned.

Platinum and its alloys can usually be safely heated for long periods in contact with the more refractory oxides without serious risk of contamination. The embrittlement which sometimes occurs when platinum wires are heated in contact with alumina insulators under reducing conditions at temperatures above 1200°C is caused by siliceous impurities in the refractory (1, 2) and platinum has been successfully melted in pure alumina crucibles in air, and in vacuum, for many years.

Inexplicable failures of high temperature apparatus are, however, occasionally en-

countered and although such contamination problems have been studied by several investigators (3, 4) few general conclusions have been arrived at. Most of the reactions observed were caused because either the platinum or the refractory oxide had been accidentally contaminated by materials which were not intentional constituents of the experimental environment, and the importance of vapour phase reactions which transmit volatile suboxides and sulphides over distances of several inches is now well appreciated (5).

This article describes some of the more interesting results obtained during a series of systematic experiments in which every effort was made to avoid the complications of spurious contamination. In view of the successful attainment of this objective, a brief description of the apparatus employed may be of value.

The basic test cell employed ensured that the platinum metal or alloy and the refractory oxide immediately surrounding it were the only two components at the experimental temperature.

The body of the cell shown in Fig. 1 is made of Pyrex glass and remains fairly cool throughout the experiment. The wire specimens are conveniently tested in the form of thermocouples which are directly heated by mains frequency alternating current, the thermocouple hot junction being immersed below the surface of a fairly loose bed of the powdered refractory under test. By using a polarised relay the heating current can, when required, be momentarily interrupted every half cycle so that the hot junction temperature can be monitored with a potentio-

meter. The circuits employed for self-heated thermocouples of this type have been described by Welch (6, 8) and others (7).

The impurities present in the oxide refractories used in this series of tests are given in the table. The platinum and platinum alloy wires conformed to the normal standards of thermocouple purity.

Effect of Atmosphere

Rhodium-platinum alloys were the first to be systematically tested in this apparatus and the protective atmosphere employed was argon containing approximately 50 p.p.m. of impurities. Under such conditions the standard platinum: 13 per cent rhodium-platinum thermocouple survived 1000 hour test runs at 1600°C with little change in output and no significant changes in the composition of either limb were detected after such periods of test. Some aluminium contamination was detected after prolonged testing at 1700°C, but this was not severe and had little effect on the output of the thermocouple.

When molybdenum-platinum thermocouples were tested in this apparatus, however, fairly severe surface erosion was encountered after the wires had been held at 1600°C for a few hours only. As oxygen was suspected as being the main cause of this effect, some of the test cells were fitted with zirconium filaments, which by electrical heating functioned as getters about 2 in. above the surface of the refractory bed.

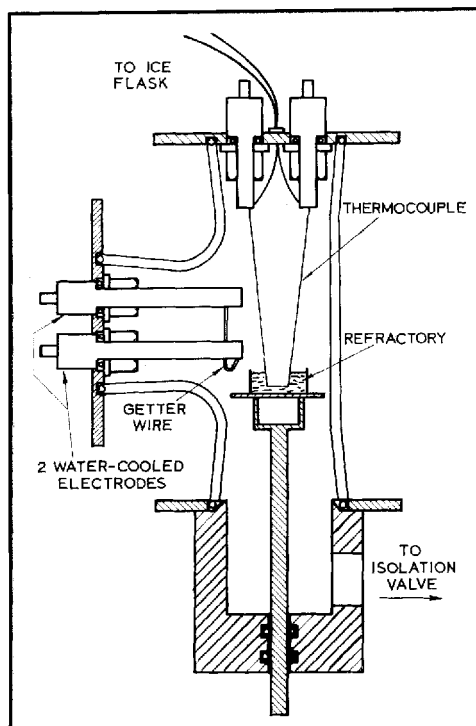


Fig. 1 Experimental test cell arrangement for studies of the compatibility of platinum with refractory oxides

Rapid failure was soon encountered when tests were made in this purified argon atmosphere. The platinum wires tended to fuse after two or three hours at 1600°C, because of severe reactions between platinum and the refractory oxide. Large volumes of oxygen were evolved by the refractory and adsorbed by the filament, while the platinum wires dissolved substantial quantities of

Typical Analyses of Refractory Oxides Used for the Compatibility Tests								
Refractory Oxide	Impurity Content in p.p.m.							
	Si	Fe	Al	Mg	B	Ag	P	Hf
Al ₂ O ₃	5	5	—	3	2	1	n.d.	n.d.
ZrO ₂	10	3	2	1	n.d.	n.d.	n.d.	<200
MgO	2	10	10	—	2	1	n.d.	n.d.
ThO ₂	8	10	n.d.	2	n.d.	10	n.d.	n.d.

n.d. - Not detected

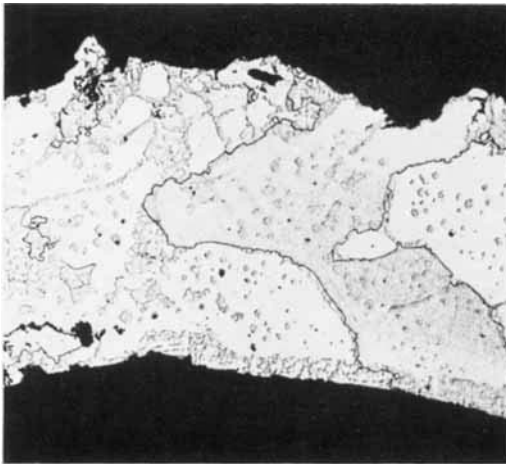


Fig. 2 Microstructure of a 1% molybdenum-platinum wire which fused after 2 hours at 1600°C in alumina under a gettered argon atmosphere. $\times 250$



Fig. 3 Microstructure of a pure platinum wire which failed after 15 hours in alumina at 1400°C under gettered argon. $\times 150$

aluminium thus forming alloys of low melting point.

These reactions were not confined to molybdenum-platinum alloys and systematic testing showed that they occurred whenever platinum or platinum alloys were heated in contact with powdered alumina under a highly purified argon atmosphere. Figure 2 illustrates the microstructure of a 1 per cent molybdenum-platinum wire which fused after two hours at 1600°C under such conditions. Depending on the area studied the contaminated wire below the refractory contained 0.5 to 1.5 per cent by weight of aluminium.

Failure was less rapid at lower temperatures, and the combination of increased time and lower temperatures allowed thermocouple wires to take up rather more aluminium. Figure 3 illustrates the microstructure of the fused zone of a 13 per cent rhodium-platinum thermocouple which had failed in gettered argon after 15 hours at 1400°C. The portion of wire in this photograph contained 2 to 3 per cent by weight of aluminium. At 1200°C reactions still occurred although contamination with aluminium was most severe in portions close to the surface of the alumina bed. Figure 4 shows the extent of the contamination observed in this region where

the wire temperature, appreciably below that of the hot junction, was about 1100°C.

Experiments in Vacuum

Since these reactions appeared to be associated with the removal of oxygen from the test cell atmosphere, it seemed reasonable to assume that they would occur in vacuum as well as in pure argon. As platinum can be safely melted in vacuum in alumina crucibles without serious contamination this conclusion seemed a little anomalous but it was decided to investigate any solid state reaction which might occur. The preliminary vacuum tests were made in the standard test cells, which were continuously evacuated by an oil diffusion pump to pressures of the order of 10^{-5} Torr as measured by a cold cathode ionisation gauge.

Reactions did occur in vacuum although they were rather less rapid than those observed in argon and somewhat different in character. Whereas in argon the attack had been fairly uniform along the submerged length of the test wire, the severe reactions in vacuum conditions were confined to those portions of the wire immediately below the refractory surface. This effect is illustrated in Fig. 5 which shows the reacted region of a

molybdenum-platinum thermocouple wire after contact with alumina powder for 100 hours at 1600°C in vacuum. Depending upon the area analysed, this reacted zone in the 1 per cent molybdenum-platinum limb contained 0.4 to 1.4 per cent by weight of aluminium.

For some time the reasons for this region of local attack at the refractory surface were not fully appreciated and it was felt initially that the oxidising potential in vacuum might possibly, although this was thought unlikely, be rather higher than that obtained in argon. Further vacuum tests were made therefore with the zirconium getter filaments in operation immediately above the refractory bed, but the results obtained were invariably the same as those encountered in the un-gettered vacuum.

Mechanisms of Dissociation

Two extreme conditions can be distinguished when the dissociation of refractory oxides is considered. It can, for example, be postulated that the dissociation of alumina results in the formation of aluminium metal and oxygen. In this instance the metal will have unit activity and we must envisage partial pressures of oxygen which at 1600°C

will be of the order of 10^{-21} atmospheres. It was difficult to believe that such low oxygen pressures had been achieved in simple experimental apparatus of the above type.

A more realistic approach involves a process of dissociation which yields both aluminium and oxygen in gaseous form. The saturated vapour pressure of aluminium at 1600°C is approximately 1 Torr. Lower pressures of aluminium would therefore at this temperature behave as superheated vapours, and on this basis, oxygen and aluminium vapour pressures of the order of 10^{-10} atmospheres would in combination satisfy the conditions necessary for dissociation. If the aluminium vapour pressure is maintained continuously at this low level we must conclude that the activity of aluminium dissolved in platinum is very low indeed. The reduction of alumina by hydrogen in the presence of platinum has been reported (9).

Considerations of this sort suggested that experiments should be made on a refractory oxide for the metal of which platinum had a higher affinity than it had for aluminium.

Platinum-Zirconia Reactions

An important feature of the Engel-Brewer theory (10) is the prediction of strong

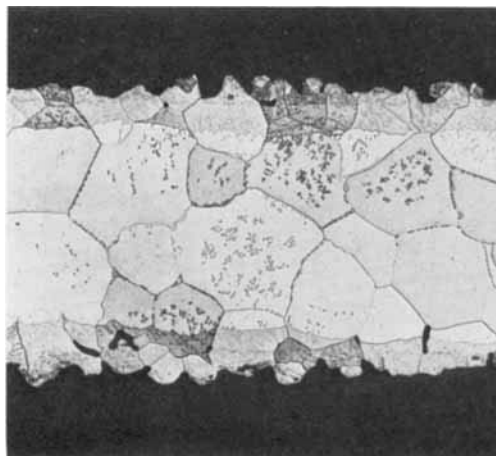


Fig. 4 Contamination in a 13% rhodium-platinum thermocouple wire after heating in alumina under gettered argon for 126 hours at 1200°C. $\times 150$

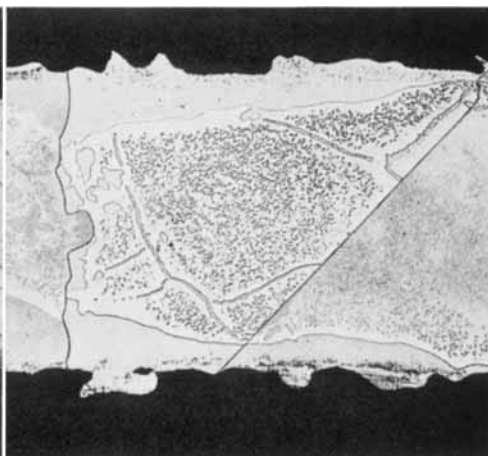


Fig. 5 Reacted zone of a 1% molybdenum-platinum thermocouple wire after immersion in alumina powder for 100 hours at 1600°C in vacuum. $\times 250$

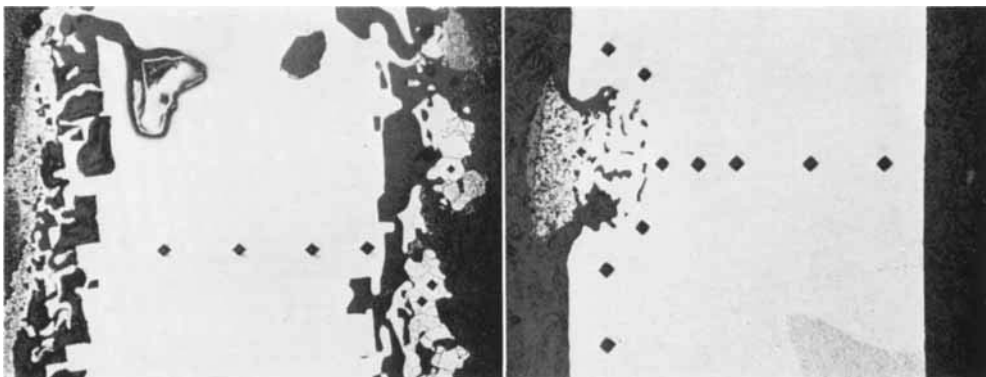


Fig. 6 Reactions between a platinum wire and zirconia powder after heating for 300 hours at 1100°C in gettered argon. $\times 180$

Fig. 7 Local surface reaction between a platinum thermocouple limb and a large zirconia particle after 300 hours at 1100°C in gettered argon. $\times 180$

reactions between elements from opposite ends of the second and third long periods of the transition series. These transition element reactions should, it was felt, provide powerful driving forces for platinum/refractory oxide reactions, and it was decided to experiment with zirconia which, when considered in isolation, is a more stable oxide than alumina. Zirconium metal has moreover a vapour pressure which is negligible compared to that of aluminium, and it was hoped that differences in the ways in which zirconia and alumina reacted with platinum might lead to a better understanding of the processes involved.

The experiments did in fact confirm a very high affinity of platinum for zirconium. When platinum and zirconium were heated together in the argon arc furnace in proportions suitable for the formation of the compound Pt_3Zr the reactions observed were comparable in intensity to Thermit reductions although not quite so violent.

When platinum thermocouples were heated in contact with zirconia powder under gettered argon severe reactions occurred at temperatures as low as 1100°C. As in the alumina experiments the vacuum reactions although severe were rather slower than those in argon. Whereas in alumina most of the reactions occurred on or within the platinum wire the zirconia reactions tended to occur

some distance away from the wire surface as shown in Fig. 6. Platinum vapour was obviously moving outwards and reacting with the zirconia particles. In regions of severe attack fairly thick layers of the compound Pt_3Zr were deposited all over the zirconia particle surfaces.

Zirconia-platinum reactions were, however, not entirely confined to those regions away from the wire surface. Where fairly large particles of zirconia were definitely in physical contact with the wire surface severe local attack occurred. Figure 7 illustrates such a region where the reaction appears to have progressed by solid state diffusion processes.

Platinum-Magnesia Reactions

Although magnesia is a very stable refractory the vapour pressure of magnesium is very much higher than that of aluminium. Surprisingly enough very few signs of reactions between platinum and magnesia have been detected even under conditions of very low oxidising potential where disastrous failure would have occurred in alumina after only a few hours at temperature.

After 100 hours of test at 1650°C in magnesia, under an atmosphere of gettered argon, the calibration of a standard platinum 13 per cent rhodium-platinum thermocouple changed by less than 1°C when retested at the gold point.

A similar thermocouple was run for 450 hours at 1650°C in magnesia under purified argon. Recalibration at the palladium point indicated a decrease in output equivalent to 4°C, which at this temperature cannot be considered a serious deterioration. Under similar conditions of test thermocouples immersed in alumina remain intact for a few hours only.

It can be concluded, therefore, that the affinity of platinum for magnesium is obviously much lower than its affinity for aluminium. Although aluminium is rapidly taken up from vapours having pressures of the order of 10^{-10} Torr, few signs of magnesium contamination have been detected even when magnesium vapours of the order of 10^{-7} Torr must have been present in the vicinity of the platinum wire surface.

Platinum-Thoria Reactions

The extremely high free energy of formation of thorium oxide and the relatively low vapour pressure of thorium metal made this compound a logical refractory for detailed examination. The preliminary test results, however, provided a good illustration of the confusion which can be introduced into studies of this sort by accidental and unexpected contamination. Platinum-rhodium thermocouples heated in the first test batches of this oxide failed catastrophically in a commercially pure argon atmosphere after only a few hours. Careful metallographic examination and analysis of the fused zone on the platinum wires revealed eutectiferous networks within the microstructure similar in appearance to those which occurred when platinum reacted with pure thoria. In addition to thorium, high concentrations of phosphorus were detected in these networks and it was subsequently found that interactions of this type could be promoted by phosphorus concentrations in the refractory as low as 75 p.p.m. At lower concentrations of phosphorus platinum-thoria reactions did not occur in commercially pure argon atmospheres.

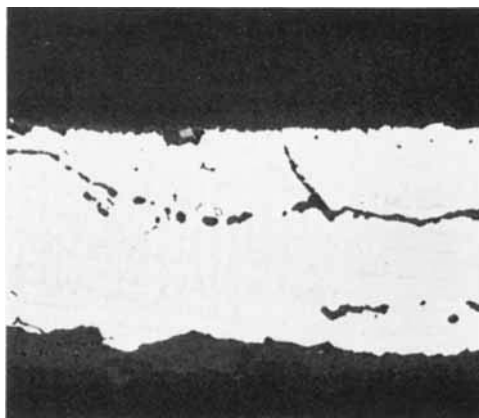


Fig. 8 Reaction between a platinum wire and thoria powder after heating for 84 hours at 1700°C in vacuum. $\times 150$

In vacuum and gettered argon, however, severe reactions were encountered. The character and intensity of the reactions were similar to those which occurred with alumina. Figure 8 illustrates the microstructure of a platinum wire after exposure to pure thoria under a continuously pumped vacuum for 84 hours at a hot junction temperature of 1700°C. The section shown was taken from a portion of wire close to the surface of the refractory bed where the most severe reaction had taken place. The thorium concentration in this area was approximately 3 per cent by weight. These reactions occurred at the wire surface and not on the surface of the oxide particles as in zirconia. While the reactions between thoria and platinum are more complex than those encountered with other oxides, there is no doubt that platinum reacts with pure thoria in atmospheres having far higher oxygen concentrations than those which would prevent any reaction with alumina and zirconia. Experiments with thoria particles covering a wide size range have shown that the alloying effects are due to vapour phase reactions although the vapour species involved have not yet been identified.

The affinity of platinum for thorium appears, therefore, to be higher than its affinity for aluminium and zirconium, a

finding very much in line with the Brewer predictions.

Conclusions

The work described above has shown that at high temperatures platinum will react strongly with refractories such as alumina, zirconia and thoria when oxygen is effectively removed from the surrounding atmosphere. Magnesia is the only refractory so far examined which resists this type of decomposition, which can occur at temperatures as low as 1200°C.

The intensity and rate of these decomposition processes depends upon the geometry and environment of the reacting system. These subjects and their practical implications will be discussed in subsequent articles.

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Strength and Ductility of Iridium

CAUSES OF FABRICATION DIFFICULTIES

Iridium is harder and more difficult to work than any of the other face centred cubic metals and, although it has a high shear modulus and low Poisson's ratio, these factors alone do not account for the troublesome fabrication characteristics of this refractory noble metal.

The anomalous deformation behaviour of iridium has stimulated a good deal of investigation, and a recent paper (1) presents the results of tensile tests carried out in the Cavendish Laboratory at Cambridge on single crystal test pieces which were pulled at temperatures ranging from 20 to 2040°C.

Test pieces were prepared by electro-spark machining from zone-refined rods which had been remelted up to 25 times, in vacuum, to expel all the dissolved and entrapped gases. The critical resolved shear stress of these carefully refined crystals was approximately seven times higher than that of iridium of comparable purity, reported upon by Haasen (2) in 1965. The rate of work hardening was, however, much less. The Cambridge investigators find it difficult to account for these differences in terms of deformation mechan-

isms, and although microscopic deformation twinning was observed, the stress-strain curves showed that this had no significant effect upon the macroscopic behaviour.

Like all previous workers, therefore, the authors of the present paper conclude that the difficulty in fabricating iridium is associated with the presence of impurities. The segregation to grain boundaries of interstitial impurities is suggested as a possible reason for the poor ductility of polycrystalline iridium, although the capricious behaviour of single crystals still remains unexplained. Although the practical fabricator of iridium will find little in the paper to assist his activities, possible lines for future investigation can be discerned from the experimental results. It seems obvious, however, that a significant "breakthrough" has yet to be achieved.

A. S. D.

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