

# Behaviour of the Platinum Metals at High Temperatures

By A. R. Powell, F.R.S.

*An important factor in the utilisation of the platinum metals at high temperatures is the loss in weight that occurs to some degree due to oxidation and volatilisation. The author critically reviews recent work on this subject and describes some original experimental work.*

It is well known that palladium and rhodium, when heated in air, become coated with films of oxide and that these oxide films dissociate at higher temperatures. Wöhler and Müller (1) state that rhodium monoxide is completely dissociated above 1127°C, and Wöhler and Witzmann (2) report that palladous oxide reverts to metal above 870°C.

Of the six metals of the platinum group, platinum alone remains untarnished on heating in air at all temperatures under ordinary conditions, although Wöhler (3) claimed to have produced temper colours on platinum foil by heating it for 16 days at 420–450°C. Since this observation was made as long ago as 1903 and has not been confirmed by later work, it may well be that the platinum used in the test was not of the highest purity and the colours were due to oxidation of impurities slowly diffusing to the surface.

Prolonged heating in air of all the platinum metals results in more or less rapid loss in weight at temperatures above about 1000°C; since this loss does not occur in inert gas atmospheres it has been attributed to the formation of volatile oxides. This is certainly true for osmium and ruthenium which form extremely volatile tetroxides, but so far the oxides responsible for the volatilisation of the other members of the group have not been isolated and identified.

In 1912 Sir William Crookes reported that a 10 g. platinum crucible lost weight continuously when heated in a stagnant

atmosphere in an electric furnace at 1300°C; after 30 hours the loss amounted to 0.33 per cent and the cooler parts of the furnace were coated with a deposit of minute hexagonal plates of platinum. No loss occurred in 20 hours at 900°C. Under the same conditions a 2 g. rhodium crucible lost no weight in 20 hours at 900°C, but 0.13 per cent in 30 hours at 1300°C. The loss in weight of both metals at 1300°C was ascribed to sublimation of the metal.

## Effects of Heating in Oxygen

In a recent paper Dr. Ernst Raub and Dr. Werner Plate (5), of the Forschungsinstitut für Edelmetalle, Schwäbisch Gmünd, report the results obtained in a study of the behaviour of rhodium, palladium and platinum in oxygen at temperatures between 900° and 1300°C. At 1100°C rhodium sheet becomes coated with a thin film of oxide, the increase in the weight of the sheet due to the oxide film reaching a maximum of about 8 mg per sq. dm of surface in about 12 hours and then remaining constant. At 1200°C there is an initial gain in weight (about 1 mg per sq. dm) in the first hour or so and then a steady and practically linear decrease in weight of nearly 2.5 mg per sq. dm per hour. At 1300°C the metal begins to lose in weight immediately and the loss increases linearly with time at the rate of 6 mg per sq. dm per hour. When sheet which has been subjected to this treatment is subsequently heated in a

high vacuum at a lower temperature there is a further loss in weight of 0.02 mg per sq. dm, equivalent to 1.56 mg per 100 g of rhodium. The authors consider that this further loss represents the solubility of oxygen in rhodium at 1300°C, but it might equally well be due to thermal dissociation of a surface film of oxide so thin as to be invisible or to dissociation of oxides of base metal impurities. No analysis of the rhodium used in the tests is given.

Although palladous oxide dissociates completely at 870°C, a sheet of palladium heated in oxygen at 1200°C gains in weight by about 0.1 per cent in the first hour due to absorption of oxygen without formation of a superficial film of oxide. On more prolonged heating at this temperature there is a slow loss in weight due to volatilisation. At 1300°C in oxygen the weight of a palladium sheet increases by about 0.08 per cent in the first half-hour and then decreases linearly with time, the original weight being reached in about five hours. At 1100°C there is a gain in weight of 0.05 per cent in five hours, after which the weight remains almost constant. At 900° and 1000°C the increase in weight is 0.007 per cent in one hour and 0.015 per cent in four hours respectively, and more prolonged heating at either of these temperatures produces no further change in weight. If sheet is heated to 1200°C in oxygen until the maximum 0.095 per cent of oxygen is absorbed and then allowed to cool to 550°C, 0.037 per cent of the gas is still retained; on slow cooling to room temperature 0.028 per cent of oxygen remains but some of this may be combined with the traces of base metals present. Sheet quenched directly from 1200°C very slowly evolves oxygen at room temperature, and practically all the oxygen absorbed by a high-temperature treatment of palladium in oxygen can be removed by heating the metal in a vacuum at about 800°C. These results indicate that the oxygen is present in solid solution, not as palladous oxide; this conclusion is confirmed by X-ray measurements of the lattice parameter after various heat treatments.

Although Lacroix (6) states that platinum does not begin to volatilise in oxygen below some temperature between 1000° and 1100°C, Raub and Plate (5) find that a measurable loss in weight occurs after very prolonged heating at 900°C, while at 1000°C the loss may amount to a few mg per sq. dm of surface in 24 hours and is about 15 mg per sq. dm at 1100°C in the same time. At 1200° and 1300°C the loss in weight of a platinum sheet heated in oxygen increases linearly with time, reaching 65 and 120 mg per sq. dm respectively in 24 hours. Comparing the behaviour of these three metals in oxygen at high temperatures the authors conclude that platinum is the most, and palladium the least, volatile at temperatures up to 1200°C, whereas at 1300°C there is relatively little difference in the volatility of all three. The graph shown opposite illustrates these results.

### **Influence of Alloying Additions**

The volatility of platinum in oxygen at 900–1100°C is appreciably reduced by alloying it with palladium or rhodium. The 10 per cent rhodium-platinum alloy loses about 240 mg per sq. dm in ten days at 1100°C and 90 mg per sq. dm at 900°C, whereas the corresponding figures are 190 and 0 for the 30 per cent rhodium alloy, 200 and 30 for the 10 per cent palladium alloy, and 110 and 10 for the 30 per cent palladium alloy. On the other hand, iridium-platinum alloys suffer much greater losses in weight on heating in oxygen than does pure platinum owing to the greater ease with which iridium oxidises and to the relatively high volatility of iridium oxide. Thus, even at 900°C the 30 per cent iridium-platinum alloy loses about 400 mg per sq. dm in 24 hours, while the 20 per cent iridium alloy loses about 200 mg per sq. dm in 36 hours.

### **Practical Importance in High Temperature Applications**

The rate of oxidation and volatilisation of platinum, rhodium and palladium in air is, of course, very much less than in pure

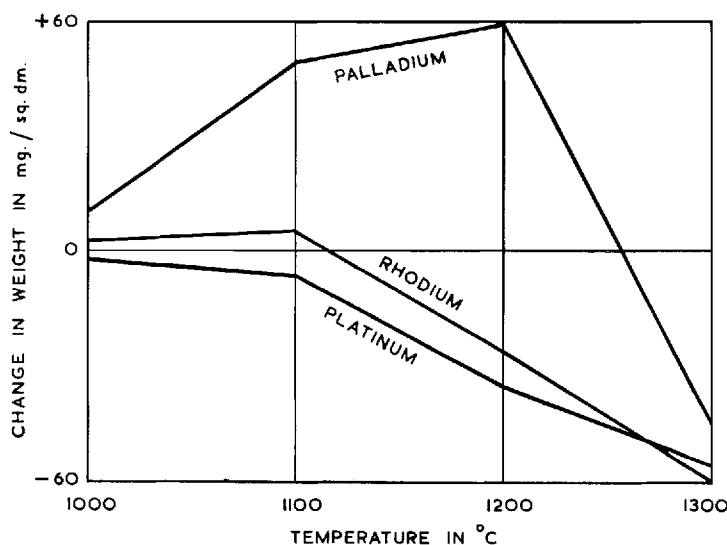
oxygen, but it is of considerable importance in the utilisation of platinum and rhodium and their alloys in high-temperature work. The three principal high-temperature applications of these metals are for thermocouples, for resistors in electric tube and muffle furnaces, and for the troughs used in the production of fibre-glass. In the last-named application the trough is surrounded by steam during use and, although some air is undoubtedly present, the partial pressure of oxygen in the gas stream is so low that practically no loss of metal by volatilisation occurs. In the absence of steam, however, very serious volatilisation of the platinum can occur as has been demonstrated by some experiments carried out in the Johnson Matthey Research Laboratories some time ago.

### Troughs for Glass Fibre Production

In these experiments troughs of platinum and of 10 per cent rhodium-platinum alloys were heated electrically inside a vertical chimney of refractory brick and maintained at 1450°C for seven weeks. The white-hot metal induced a strong upward current of air which swept away any vapours given off by the metal and these then condensed in the cooler part of the chimney above and around

the trough. At the end of the test the trough had lost about 4.7 per cent of its original weight, a bright crystalline metallic deposit had built up on the walls of the refractory surrounding the trough and, in some tests, this crystalline deposit had formed a bridge between the trough and the chimney walls. The crystalline deposit consisted of well-defined cubes and hexagonal plates, some of which had sides several millimetres long; the crystals produced from the platinum trough were pure platinum and those from the alloy trough were platinum with 10.05 per cent of rhodium.

In the cooler zone of the chimney above the crystalline deposit there was a considerable amount of black amorphous deposit which contained about 3 per cent of oxygen irrespective of whether the trough was pure platinum or the 10 per cent rhodium alloy; the platinum:rhodium ratio in the black deposit obtained from the alloy contained the two metals in an almost exactly 9:1 ratio. These results indicate that volatilisation of both metals in air at 1450°C occurs as the result of the formation of a volatile oxide and that no preferential volatilisation of either platinum or rhodium takes place in air at this temperature. The volatile oxide appears to dissociate completely in the hot zone (1200–



*Change in weight of rhodium, palladium and platinum on heating for 10 hours in oxygen (Raub and Plate)*

1300°C) from the more concentrated oxide vapours, but in cooler parts (700–800°C) of the refractory a considerable portion of the deposit consists of oxide, even when rhodium is absent. According to R. Lacroix (6) the oxide produced by volatilisation of platinum in air contains platinum and oxygen in the atomic ratio of 2:1, i.e. the deposit should contain 3.94 per cent of oxygen. Since only 3.1 per cent was found it is probable that some dissociation occurred owing to the high temperature of the refractory on which it was deposited.

### Improvement in Life of Platinum-wound Furnaces

Early tube and muffle furnaces wound with platinum wire resistors packed loosely in kieselguhr frequently failed after more or less prolonged use at high temperatures by thinning of the wire due to volatilisation of the heating element. Examination of the refractories after failure generally disclosed crystalline deposits of platinum on the tube and in the surrounding refractories and packing material. In modern furnaces of these types the platinum, rhodium-platinum or pure rhodium wire heating element is embedded in the alumina refractory and the whole is pre-fired to form a monolithic element with the wire resistor completely surrounded by fired alumina. This has the effect of preventing even slow circulation of air over the bare wire and consequently prevents its oxidation and volatilisation, thus ensuring a much longer life for the furnace

and the ability to operate it at higher temperatures without fear of premature breakdown. The design of this type of furnace was recently described by Priddis (7).

### Rate of Volatilisation of Thermocouples

Thermocouples consisting of platinum:rhodium-platinum wires are well known to suffer small changes in calibration after prolonged heating at high temperatures. If the couples are protected with suitable refractory sheaths which prevent a rapid circulation of hot air over the metal the rate of volatilisation of the metal is very small, but quite serious losses in weight can occur if the bare wires are heated in contact with a moving air stream for long periods. McQuillan (8) reported a loss in weight of over 10 per cent to occur in 22 hours at 1600°C with a platinum:13 per cent rhodium-platinum couple; since at this temperature both wires probably volatilise at similar rates the composition of the vapour produced will be intermediate between that of the two wires and any deposition of metal on the wires is likely to cause changes in composition and hence a change in the calibration of the couple. With a non-porous refractory tube surrounding the couple the air is kept stagnant and the rate of volatilisation considerably reduced but not altogether eliminated. The effect of prolonged heating of thermocouple wires at high temperature is discussed at some length by Bennett in his book on "Noble Metal Thermocouples" (9).

### References

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