

Reactions of Oxygen with the Platinum Metals

III—THE OXIDATION OF PALLADIUM

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In the third and concluding part of this survey of the changes that occur when the platinum metals are heated in oxygen at temperatures up to their melting point the behaviour of palladium is considered. The gain in weight when commercial palladium is heated to around 1000°C in air or oxygen, reported by many experimenters, is probably the result of the internal oxidation of base metal impurities. At higher temperatures, the primary cause of the loss of weight then observed is almost certainly the very high vapour pressure of palladium itself. The reaction between palladium vapour and oxygen to form PdO gas has yet to receive the experimental study it demands.

The behaviour of palladium when heated in air or oxygen, particularly to temperatures over about 1000°C, is far less well established than that of the other platinum metals discussed in the earlier parts of this review (1); moreover, many of the statements to be found in the literature do not really stand up to critical examination.

At temperatures up to about 800°C, palladium appears to be very similar to rhodium in its reactions with air or oxygen. An oxide skin of PdO forms on the surface, thickening as the temperature and the time of heating are increased. When a sample heated in the temperature range from about 400 to about 850°C is cooled either slowly or by

quenching, the tarnish film is plainly visible to the eye, as is well known to all who have ever annealed the metal.

It thus seems to be reasonably certain that although the film of PdO is not particularly protective, it is sufficiently so to resist any form of scaling; the film never flakes away, nor is its formation accompanied by any appreciable increase in weight.

At a temperature of about 870°C the oxide film formed in oxygen at a pressure of one atmosphere becomes unstable as a solid and at higher temperatures a clean metal surface is in equilibrium with the surrounding oxygen. In this respect, palladium behaves like all the other platinum metals.

It would thus be expected that at temperatures above 870°C palladium would tend to lose weight, like the other platinum metals, through formation of a volatile oxide.

There is, however, ample good experimental evidence that at temperatures slightly over the decomposition temperature commercial palladium samples actually gain in weight. Raub and Plate (2), for instance, the distinguished experimenters at the Forschungsinstitut für Edelmetalle of Swäbisch Gmünd, give the curves shown in Fig. 1 for palladium heated in oxygen at 900°C and 1000°C.

These results are, to say the least, unexpected. At these temperatures palladium is seen to increase slightly in weight quite rapidly, gaining at 900°C about 0.007 per cent in a little over an hour and at 1000°C about 0.015 per cent in four hours. Thereafter, on longer heating, the weight remained virtually

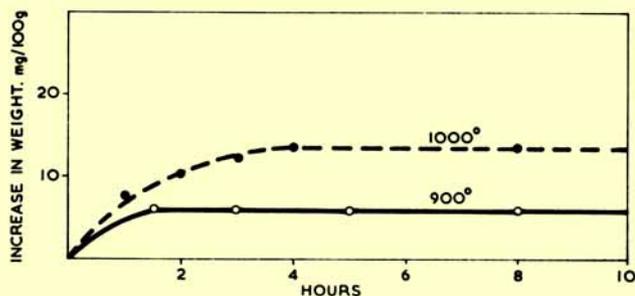


Fig. 1 Changes in weight of commercial palladium heated in oxygen at 900° and 1000°C (Raub and Plate)

constant, at least for up to ten hours. It is not clear whether these tests were made in the furnace generally used by these investigators, through which a stream of oxygen was passed at 0.4 litre/minute, or whether they were among the special tests "at low temperature" in which the specimens were hung in a vertical furnace and weighed constantly during annealing. No mention is made of any flow of gas in the latter set-up. The samples were quenched after heating and presumably were then bright and free from surface oxide.

The rapid initial increase in weight observed in these experiments is almost certainly caused by the internal oxidation of base metal impurities in the palladium (as, indeed, Raub and Plate point out). The metal used is described, rather loosely by present-day standards, as having "a purity of 99.9 per cent, the balance being composed of copper, iron, gold and other platinum group metals".

Internal oxidation of alloys of palladium with small amounts of base metals when heated in air is, indeed, frequently encountered and can be readily seen under the microscope in cross-sections cut through a treated sample. A photograph of a typical

section of palladium containing 0.2 per cent of chromium showing sub-surface or internal oxidation is reproduced in Fig. 2. If material which has been internally oxidised is subsequently heated in hydrogen, severe fissuring and surface disintegration result and all the familiar features of hydrogen embrittlement can be observed. Atkinson and Gladis (3) have described fissuring of this type after torch brazing commercial palladium (and ruthenium-palladium alloys), particularly when the parts are heated alternately in oxidising and in reducing flames.

It would thus seem very reasonable to ascribe even the largest weight increase of 0.015 per cent observed at 1000°C to the oxidation of the copper and iron present; and, further, it does not really seem unlikely that the impurities are not completely oxidised at 900°C, the reaction proceeding rather more completely at 1000°C.

If this reasoning is correct, it would be expected that very pure palladium would remain almost constant in weight at 900°C and 1000°C. Unfortunately there is no experimental evidence available to establish this conclusion.

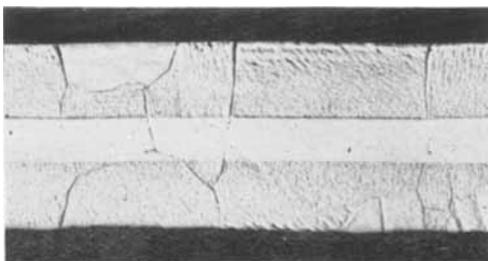


Fig. 2 Section through a sample of palladium sheet containing 0.2 per cent of chromium after annealing for ninety-six hours in air at 1000°C. Particularly evident are the sharp lines of demarcation between the outer oxidised zones and the unoxidised interior of the specimen

There is a widely held impression that oxygen can go into solution in solid palladium and it may be useful to consider critically how far this can be substantiated.

At temperatures up to, say, 800°C it is very difficult to believe that there can be any solubility at all. Palladium is widely used in this temperature range to form diffusion barriers for the purification of hydrogen, and there is ample evidence that a palladium barrier can hold back all oxygen as completely as can be detected by the most sensitive means available. Palladium-purified hydrogen certainly contains less than 0.1 part of oxygen per million and may possibly contain much less if contamination of the vessel walls on the outgoing side of the cell can be prevented. Such complete purification from oxygen would not seem to be possible if oxygen were soluble to any appreciable degree in palladium; some few atoms would almost certainly recombine at the surface and escape.

At temperatures between, say, 800 and 1000°C there is, however, the evidence that commercial, not very pure, palladium gains in weight when heated in air. It might be argued that if this is due, as suggested, to internal oxidation of impurities, this presupposes that oxygen can diffuse through palladium (and hence be soluble to at least a limited extent). However, it seems equally possible that the internal oxidation may result from the handing on, so to speak, of atoms of oxygen from neighbouring atoms of the dissolved impurity base metal, and that the pure palladium lattice itself may still be unable to accommodate atoms of oxygen in its structure.

At temperatures above 1000°C the position is much more uncertain. Raub and Plate, for instance, record experimental results showing that at 1100°C the weight increased by about 0.055 per cent after five hours, while at 1200°C the maximum increase was 0.095 per cent on samples quenched from the furnace. If these samples were subsequently heated to 500°C or were cooled slowly much of the oxygen taken up could be removed and

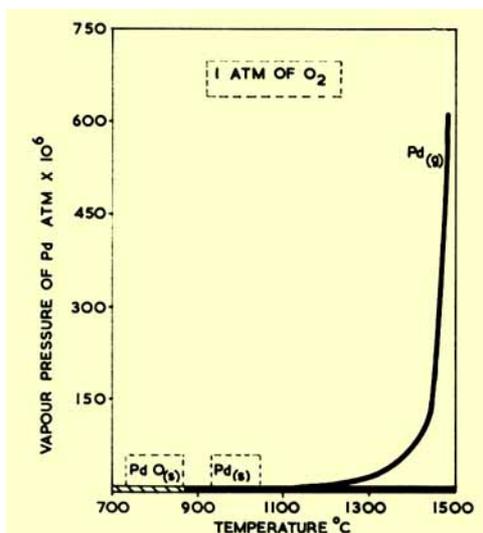


Fig. 3 Partial phase diagram for palladium in one atmosphere of oxygen, showing how vapour pressure of palladium increases rapidly with temperature. The vapour pressure curve is plotted in millionths of an atmosphere

the oxygen content reduced to 0.0283 per cent, an oxygen content that can reasonably be attributed to that needed to oxidise the base metal impurities. These authors consider that these results provide evidence that oxygen can go into solid solution into palladium at these high temperatures, but it is most desirable that similar tests should be made on very pure palladium.

To return now to consider possible reactions at the surface of palladium, it would seem reasonable to suppose that, irrespective of whether or not oxygen can dissolve in the solid metal at temperatures over about 850°C in an atmosphere of one atmosphere of oxygen, the clean palladium metal surface must endeavour to reach equilibrium with oxygen gas and PdO(g), in the same way as discussed in Part II of this review for the other platinum metals.

However, with palladium it is necessary to take into account a factor hitherto ignored as being negligible for the other metals, the vapour pressure of palladium metal itself. As

will be seen from Fig. 3, the value for this increases very rapidly, rising from 0.0063×10^{-6} atm. at 1000°C to 620×10^{-6} atm. at 1475°C ; the curve in fact following fairly closely that for the partial pressure of $\text{RhO}_2(\text{g})$ over rhodium in oxygen. The vapour pressure of palladium is about 10,000 times higher over the range 1000 to 1600°C than that of platinum or rhodium. These figures are based on the results of Alcock and Hooper (4); rather higher values for vapour pressure have been reported by earlier investigators (5).

Thus, at temperatures over, say, 1400°C , when the vapour pressure of palladium metal becomes significant, a very complex situation must exist in the boundary layer above a palladium metal surface in oxygen.

The picture that presents itself is that of a basic sandwich structure with a thin layer of metallic vapour immediately above the surface of the bright palladium metal overlaid by perhaps a thicker layer of PdO gas and both underneath a blanket of oxygen. There will be mixing and diffusion between the layers and it is inevitable that the rate at which palladium solid will lose weight will depend very greatly upon conditions within the heating chamber.

Thus without a good deal of careful experimental work it is not possible to be at all specific regarding the manner in which palladium is oxidised at high temperatures. We do not even know the partial pressure of the PdO gas that is certainly present in these conditions.

Correction

In Part I of this series it was stated that the dissociation temperature of the surface oxide film on platinum corresponds to the temperature at which the vapour pressure of the oxide becomes greater than the vapour pressure of the metal. On further consideration the author finds that this cannot be sustained as a general principle and there are no experimental values for the vapour pressures of platinum and its oxide at this temperature. Those who have a copy of Part I available might care to delete the sentences on pages 51 and 53 which make reference to this matter.

References

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Precipitation in Gold-Platinum Alloys

THE EFFECTS OF ATMOSPHERES

According to some recent observations of Dr Reinacher (*Zeitschrift für Metallkunde*, 1965, **56**, 216), the presence of oxygen has a profound effect upon the mode of precipitation of the gold-rich phase from supersaturated gold-platinum solid solutions. The alloys studied, which contained 8 to 10 per cent by weight of gold, were produced by induction melting under argon in alumina crucibles. When solution treated and aged in hydrogen the test specimens attained a maximum hardness after less than one hour at 600°C . They over-aged rapidly and reverted to the quenched hardness in less than ten hours. Specimens heat treated in air rather than in hydrogen maintained surface hardnesses in excess of 250 HV even after 25 hours at 600°C . This over-ageing effect was caused by the

formation of a coarse lamellar precipitate on the surface of the hydrogen-treated specimens. As Reinacher suggests, this may be due to surface hydrogen penetration which, by distorting the lattice, affects the solubility of gold in platinum. An alternative explanation might be that surface oxygen penetration increases the solubility of gold in the lattice and therefore inhibits precipitation. It is certainly true to say, however, that in a system of this type with two phases of very similar thermodynamic stability, effects are likely to make themselves apparent which would be completely masked in other alloys. This characteristic could make the gold-platinum system useful for a variety of fundamental investigations.

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