The Oxidation of the Platinum Metals

A DESCRIPTIVE SURVEY OF THE REACTIONS INVOLVED

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On gentle heating in air or in oxygen all six of the platinum metals develop thin tarnish films, visible or invisible, on their surfaces. On exceeding individual critical temperatures these films disappear, exposing clean metal, the change having the characteristics of a low-energy phase transformation. The mechanisms involved are examined in this survey and their effects on the stability, strength and surface reactivity of the platinum metals and their alloys are discussed.

It is little short of a hundred years ago that Thomas Alva Edison first reported (in 1879) that heated platinum wires lost weight many times more rapidly in air than in vacuum. Ever inventive, he suggested that the effect was the result of "air washing" by convected currents of air which mechanically carried away particles from the soft glowing surface.
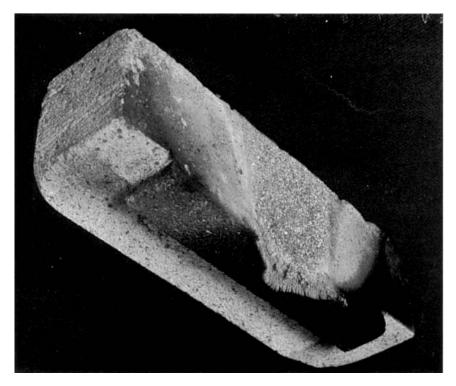
Today it is well established that the higher losses in air are bound up with the formation of an oxide of platinum which is very much more volatile than is the metal at high temperatures. The mechanisms involved in the reaction are, however, complex and continue to be a fascinating and sometimes a rewarding study for the user of platinum.

The experimental data available on the oxidation behaviour of platinum and the other platinum group metals were reviewed by the present writer in three articles in this journal a little over ten years ago (1). Not a great many observations have been recorded since then, but in the intervening years some of the uncertainties in the original papers have been clarified. The present paper is an attempt to give a unified account of the reactions involved.

When platinum is heated in air or oxygen up to a temperature at which it glows with a dull-red colour it, like gold, undergoes no visible change. The alchemists would have said that it remains noble. Nevertheless, it is not difficult to show that a very thin film of transparent solid oxide can form on its surface—probably having the composition PtO_2—and that this thickens as the temperature is raised.

The chief evidence for the existence of this film derives from electrochemical observations. The film, which can be thickened by anodic oxidation in many electrolytes, can be stripped in a solution of hydrochloric acid and sodium chloride and its composition determined. Moreover, the existence of this film makes possible the dissolution in the same electrolyte of electrodes of platinum and many of its alloys by the application of an alternating potential. During one half-cycle an oxide film is formed on the surface by nascent oxygen; during the other half-cycle the oxide is dissolved.

When polished specimens of palladium, iridium, rhodium or ruthenium are similarly heated the solid oxide films form dark brown or black colorations on the surface, like the temper colours on iron. The oxide

Heavy crystalline deposits of platinum on the hotter surfaces of a refractory brick that had seen long service in a position close to the rhodium-platinum heating elements of a furnace

coatings are still very thin and adherent and once formed have every appearance of being protective in character against continuing growth on long heating.

It may thus be said that the behaviour of some of the platinum metals on heating in air or oxygen to temperatures of around 400 to 500°C is not so very different in kind from that of certain of the base metals.

At higher temperatures, however, the difference is dramatic. For each of the platinum metals there is a critical temperature or range of temperatures above which the oxide film, instead of continuing to thicken, completely disappears; and if the metal is then quenched rapidly it is seen to be bright and oxide-free. The exact temperatures of the transformations are difficult to determine and exact values have yet to be established.

In the literature there are signs of much confusion of thought in describing the nature of this change. Sometimes the solid oxide film is said to evaporate; at other times it is said to dissociate. Many find it difficult to reconcile thermal dissociation of a solid oxide with the increase in affinity between platinum and oxygen which is known to take place as the temperature is raised.

This mental block may perhaps be removed simply by considering that within the critical temperature range the oxide experiences a phase change—from PtO_2 solid direct to PtO_2 gas.

In addition, it is necessary to appreciate that at atmospheric pressures the increase in energy involved in this solid-gas phase change is extremely small; so that the partial vapour pressure of the PtO_2 gas formed is also very low. Thus there will be little driving force available to disperse the newly-liberated gaseous molecules throughout the surrounding oxygen.

The consequences of the phase change will depend on the freedom of the newly formed molecules of PtO_2 gas to escape from the vicinity of the metal surface. If the original film of solid oxide is very thin and the heating rate through the transformation slow, the partial vapour pressure of the gas may be sufficient to disperse the molecules throughout a quiescent surrounding atmosphere of oxygen. In a turbulent atmosphere, greater amounts would be swept away. In these conditions the effect is as if the solid oxide had evaporated.

If the oxide films are thicker, and molecules of PtO_2 may be unable to disperse, then the partial vapour pressure of PtO_2 gas above the surface will exceed the equilibrium value. The layer will be super-saturated in PtO_3 gas. Since PtO_2 solid cannot exist above the critical temperature, the only way in which equilibrium can be restored is for some platinum metal to be deposited. The effect in these conditions is as if the solid oxide had dissociated.

The mechanisms which govern the rate at which the gaseous oxides form and diffuse away from an electrically heated wire or ribbon of platinum have been studied by several investigators. In particular George C. Freyburg, of NASA Lewis Research Center, Cleveland, Ohio, has examined the losses of weight of ribbons or wires of various sizes when heated by the passage of an electric current in oxygen at pressures of 0.025 to 1000 Torr (2). He has shown that the rate of oxidation is determined by the rate of escape of oxide molecules through the boundary layer away from the platinum, and not by diffusion of oxygen through the layer towards the metal.

In his discussion, Freyburg points that as the pressure of oxygen increases the gaseous oxide molecules formed at the wire surface suffer collisions at distances closer and closer to the ribbon and ... "any oxide molecule that is back-reflected is decomposed on the hot ribbon; the platinum is redeposited on the platinum surface". Stated in this way, it must appear paradoxical that a molecule of PtO_2 formed at the hot Pt surface should be decomposed on its return. It would appear more acceptable to consider that returning molecules, projected into the saturated region of the boundary layer, produce such a state of supersaturation that the excess molecules are forced to deposit their platinum. It follows from this that it is not necessarily the returning molecule that is decomposed; it may very well be another which is already close to the hot wire. As the temperature is raised above the critical point, reaction becomes more vigorous, larger quantities of PtO_2 gas will be formed, and its equilibrium partial vapour pressure will increase, and provide an increased driving force for dispersion of the gas molecules. Evaporation will eventually replace decomposition.

Now consider what happens if the current through an electrically heated platinum wire is reduced. As the temperature falls, the gas layer near the wire becomes immediately supersaturated with PtO_2 gas; and as long as the temperature of the wire or surrounding refractories remains above about 400°C, then platinum metal will be deposited. On raising the current again the small amount of deposited platinum on the wire will quickly be oxidised and re-evaporated; but after repeated cycles of temperature platinum will generally build up slowly on any cooler refractory and will eventually form the familiar spangles with well-defined crystal faces which are observed in old platinum-wound furnaces.

Fluctuations in temperature may thus be an important, if often unconsidered, cause of migration of platinum in such diverse industrial applications as catalyst surfaces, hot crucibles and containers, and heating elements.

Rhodium

Of the other platinum metals, rhodium most closely resembles platinum in its behaviour at high temperature. On platinum, the thin solid oxide film persists at temperatures up to about 450°C in oxygen at a

pressure of 1 atmosphere (values ranging from 280 to 750°C have been suggested in the literature), and perhaps up to rather lower temperatures in atmospheric air. On rhodium, as was mentioned earlier, the oxide film thickens sufficiently to be visible as a tarnish after heating. The transformation temperature is much higher than for platinum and has been reported to be about 1030°C in air and 1040°C in oxygen at a pressure of one atmosphere.

Since the solid oxide remains the stable phase up to such a high temperature, a very small amount of evaporation of RhO_2 can occur below its transformation temperature. Every solid, as Robert Boyle expressed it, has its own "little atmosphere"; and although "no man has yet tried whether gold (or any other solid) may not in time lose its weight" at room temperature, when a solid becomes white hot the losses commence to become measurable.

Thus at 1000°C the partial vapour pressure of RhO_2 above a solid RhO_2 film in air is probably a little over 10^{-7} atm and only a little less than that of PtO_2 above platinum. Above the transformation temperature the partial vapour pressure probably suddenly increases; for it is known that above about 1100°C it is higher than that of PtO_2 and then increases with temperature at very much the same rate or only very slightly more rapidly.
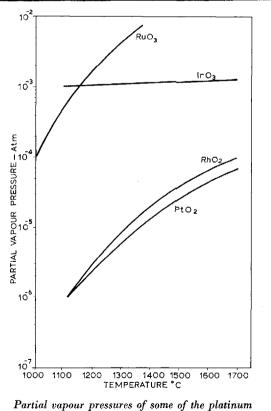
Ruthenium and Osmium

With the more reactive platinum metals, ruthenium and osmium, their reactions with oxygen are more complicated.

On heating ruthenium in air, a thin film of RuO_2 forms on the surface and becomes visible as a brown coloration above about 400°C. It is the only solid oxide that exists in equilibrium with the metal and with oxygen, and does not transform until a temperature of 1540 to 1580°C is reached in 1 atmosphere of oxygen or about 1405°C in air.

The formation of solid RuO_2 is, however, only an intermediate stage in the oxidation of ruthenium metal. The weight-losses observed when ruthenium is heated are not the result of volatisation of the solid oxide but of the formation by its further oxidation of new volatile species.

For it appears that RuO_2 cannot itself exist as a gaseous molecule. The coating of solid RuO_2 therefore reacts with the surrounding oxygen and forms new gaseous compounds—RuO_4 in small quantities at temperatures up to about 720°C, and RuO_3 at higher temperatures.

It is significant that the reactivity of RuO_2 with oxygen is exceptionally high. Even at 1000°C the vapour pressure of RuO_3 gas

Partial vapour pressures of some of the platinum metal oxides in 1 atmosphere of oxygen

formed from RuO_2 is about 200 times as great as PtO_2 gas at the same temperature and at 1300°C it is about 1000 times as great.

Osmium is much more reactive. Even at room temperatures it is covered with a layer of solid OsO_2 which reacts with the air to form the poisonous OsO_4. This has a remarkably high vapour pressure, so that finely divided osmium powder loses weight at a measurable rate.

Iridium

Not a great deal of experimental evidence is available on the exact mechanism of the oxidation of iridium. Like ruthenium, iridium becomes covered with a layer of the dioxide, but this seems to be a little less stable than RuO_2. There are indications that IrO_2 may start to decompose with formation of an oxygen-deficient non-stoichiometric compound at a temperature above about 1050°C; and it transforms to IrO_3 at about 1115°C under a pressure of oxygen of 1 atmosphere or at about 1020°C in air.

The formation of IrO_3 may well involve an appreciable energy change, since the partial vapour pressure of IrO_3 gas at the temperature of its formation is remarkably high—of the order of 10^{-3} atm. It has for long, indeed, been recognised that iridium loses weight at a measurable rate when it is heated in air to temperatures in excess of about 1100°C.

Palladium

At temperatures up to about 850°C, palladium is very similar to rhodium in its reactions with oxygen. A dark brown oxide film develops on its surface, and this vanishes suddenly when the transition temperature is exceeded.

The vapour pressure of the PdO gas formed is relatively low, but at above about 1000°C a new factor calls for consideration—the vapour pressure of the metal palladium itself. The value of this increases with rise in temperature as fast as that of rhodium oxide gas up to about 1450°C and is probably the controlling factor in determining the loss of weight of the metal when heated in air or oxygen. Reactions probably take place between Pd vapour and oxygen at high temperatures with the formation of PdO gas, but surprisingly little is known quantitatively about their mechanisms.

Oxidation of the Alloys

Industrially, the oxidation of the pure platinum metals rhodium, ruthenium, osmium and even palladium at high temperatures is of little concern; it is the performance of their generally rather dilute alloys with platinum that needs to be considered. Typically, the industrial alloys contain about 90 per cent of platinum and 10 per cent of the second platinum metal.

The first question that arises concerns the structure and composition of the oxide layers that form as the temperature is raised. They are almost certainly solid solutions of the oxides of the alloy components—double oxides of the platinum metals involved. With rhodium-platinum alloys, the proportions of platinum and rhodium in the double oxide is probably about the same as in the alloy. With alloys of platinum with iridium, rhodium, or osmium the oxide films may contain more of the reactive alloying metal than is present in the underlying alloy, and the composition may vary with temperature, but little experimental work on this has been reported.

The second question has to do with the transformation temperature of the alloy oxide film. The oxide film persists on the surface of all these alloys to an appreciably higher temperature than on pure platinum, and transformation takes place, not at one definite temperature, but over a temperature range.

The answers to both these hitherto largely neglected questions may well have a bearing on the behaviour of platinum and the platinum alloys in catalytic oxidising reactions, since they determine the nature of the

catalytic surface—whether it is bright metal or an oxide film; and if an oxide film, its composition.

At high temperatures at which the alloy surface is free from solid oxide coatings in air or oxygen there is, of course, a loss of weight due to the formation of volatile oxides. Rhodium-platinum alloys volatilise almost unchanged in composition at temperatures from about 1100° to 1800°C or higher. Over this range of temperatures the partial vapour pressure of RhO_2 is slightly higher than that of PtO_2; but the difference is not great and there is little experimental evidence of any preferential loss of rhodium. The crystalline deposits on refractories close to rhodium-platinum furnace windings are usually very close indeed in composition to that of the heating elements.

The behaviour of alloys of platinum with the more readily oxidisable metals iridium, ruthenium and osmium is, however, very different. As long ago as 1886 Le Chatelier observed that platinum thermocouples having as one leg a 10 per cent iridium-platinum alloy were prone to change their calibration in service at about 1000°C and over, and attributed this to a loss of iridium from the alloy. His recommendation that rhodium-platinum alloys were to be preferred as being more stable in air at high temperatures has been followed ever since.

At above about 1200°C the differences between the partial vapour pressures in air of the oxides IrO_3, RuO_3 and OsO_3 amount to many orders of magnitude and the differences increase rapidly as the temperature is raised. The table gives approximate values at 1300°C and 1500°C.

When these alloys are first heated, selective volatilisation will start from the surface. The extent and rate of the loss depends, as has been discussed earlier, on the ease by which the volatile oxides can escape from the hot surface, and in any given environment it is reasonable to expect that it is largely a function of the partial vapour pressure of the oxide. Furthermore, the partial pressures produced by each constituent are initially in the ratio of their atomic proportions in the alloy.

As heating continues, however, the surface will be depleted of the most volatile components and a diffusion gradient will be set up within the alloy which will control the subsequent progress of evaporation. One consequence of this outwards diffusion is the generation of vacancies which may lead to cracking and premature failure if the material is under stress.

The consequences of the selective oxidation of these alloys may well influence their behaviour as catalysts. The steady depletion of the surface in the alloying metal would be expected to result in a drift in its selectivity or activity; although in conditions of fluctuating temperature the effect may to some extent be masked by selective re-deposition from the vapour phase.

In this connection, it is of interest to speculate on the possibility of using a composite structure formed from a platinum-clad core of iridium, ruthenium or osmium. In operation, a diffusion gradient would be set up and by proper choice of platinum thickness a steady state might be achieved, the loss of alloy at the surface being balanced by material diffusing outwards from the core. Thus, at constant working temperatures, it might be possible to provide an oxide-free surface of constant composition.

| | Partial Vapour Pressures, atm. | |
	1300°C	1500°C
PtO_2	0.5×10^{-5}	1.8×10^{-5}
IrO_3	110×10^{-5}	130×10^{-5}
RuO_3	500×10^{-5}	4000×10^{-5}

References

1 J. C. Chaston, *Platinum Metals Rev.*, 1964, **8**, (2), 50–59; 1965, **9**, (2), 51–56, (4), 126–129
2 G. C. Freyburg, *Trans. Met. Soc. A.I.M.E.*, 1965, **233**, (11), 1986–1989