

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

- 1 J. C. Chaston, *Platinum Metals Rev.*, 1964, **8**, 50-59; 1965, **9**, 51-56
- 2 E. Raub and W. Plate, *Zeit. für Metallkunde*, 1957, **48**, 529-539
- 3 R. H. Atkinson and C. P. Gladis, *Metals Tech.*, 1946, (13), (3), (A.I.M.M.E. Tech. Publ., 1952)
- 4 C. B. Alcock and G. W. Hooper, *Proc. Roy. Soc. A.*, 1960, **254**, 551
- 5 R. F. Hampson and R. F. Walker, *J. Nat. Bur. Sci.*, 1961, **65A**, 289-295; 1962, **66**, 177-178

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.

A. S. D.