The Affinity of the Platinum Metals for Refractory Oxides

REACTIONS UNDER REDUCING CONDITIONS

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The presence of a platinum metal enhances the ability of hydrogen, carbon, carbon monoxide and organic vapours to reduce the more stable refractory oxides. Such reactions, which may start at temperatures as low as 600°C, occur because of the high affinity of the platinum metals for the metal of the refractory oxide and result in the formation of intermetallic compounds or stable solid solutions. This account, based on experimental studies which yielded useful information on the thermodynamic behaviour of platinum metal alloys, presents results which should assist in preventing damage to industrial platinum apparatus. It also suggests that metals could be brazed to refractory oxides using a platinum containing brazing alloy under suitable reducing conditions.

Practical experience has shown that even platinum and palladium are not completely resistant to oxidation, and that they can, under certain conditions, also react with base metal oxides at high temperatures (1–5). When heated in air some of the platinum metals, initially develop an oxide skin which disappears by dissociation or evaporation above a critical temperature. Others, such as platinum itself, retain a clean surface, but suffer a more or less rapid decrease in weight because of volatile oxide formation.

The more stable and refractory base metal oxides can also react with platinum in an argon atmosphere, in vacuum, or even in air, the reactions being particularly severe with zirconia, thoria and alumina. Under such conditions magnesia can be considered the only oxide which is truly inert with respect to platinum (3, 4). These reactions are greatly accelerated by the presence of strong reducing agents, Bronger and his collaborators (6, 7, 8) having shown that many inter-metallic compounds can be synthesised by reacting the platinum metals with oxides in a hydrogen atmosphere. Similar techniques were also used for the production of palladium-tungsten alloys (9).

Within an industrial environment strongly reducing conditions are sometimes difficult to avoid. The platinum alloy bushings used for glass fibre production provide a good example of the hazards likely to be encountered, as they can be rapidly destroyed by silicon if the glass feed is contaminated by organic residues such as oil or wood. Platinum thermocouples can also react with their refractory insulators if the assembly is accidently brought into direct contact with luminous or other reducing flames.

Following earlier studies of the reactions between platinum and the transition metal carbides (10), the programme described below was undertaken to identify those industrial situations where reducing conditions caused by the presence of carbon monoxide, carbon or the hydrocarbons, could lead to the rapid failure of platinum plant or equipment.

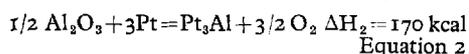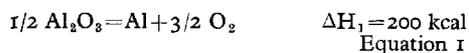|	Ruthenium	Rhodium	Palladium	Osmium	Iridium	Platinum
The Temperature of the Reactions of Platinum Metals with Oxides in a Hydrogen Atmosphere, and the Compounds Formed (8) _(Temperature in degrees Celsius)_						
Li						900 Pt_2Li
B	+1400	+1400		+1400	+1400	+1100
Si	1450 RuSi	1400 Rh_2Si	1100 Pd_2Si	—	1500 IrSi	+1100
Ti	1750 *	1600 Rh_3Ti	1200 Pd_3Ti	—	1600 Ir_3Ti	1200 Pt_3Ti
Al	—	1450 RhAl	Pd_2Al 1300 Pd_3Al_2 PdAl	—	1600 IrAl	1500 Pt_2Al_3 1250 Pt_5Al_3 1200 Pt_3Al 1100 $Pt_{13}Al_3$
Ba		—			—	1200 Pt_5Ba Pt_2Ba
Sr		—			—	1200 Pt_5Sr Pt_3Sr Pt_2Sr
Mg		—	?	—	—	1100 Pt_7Mg Pt_3Mg
Ca		—	?		—	1200 Pt_5Ca Pt_7Ca_2 Pt_2Ca
Sc		—	?	—	—	1200 Pt_3Sc
Y		—	?	—	—	1200 Pt_5Y
Cr						1000 Pt_3Cr (ordered)

+ reaction at the given temperature.   − no reaction observed.   ? reaction products not identified.   * noble metal solid solution.

Reactions in Hydrogen

The principle of these reactions is best shown by the reaction of platinum and alumina in hydrogen (6):

$$1/2\ Al_2O_3 = Al + 3/2\ O_2 \qquad \Delta H_1 = 200\ kcal$$
Equation 1

$$1/2\ Al_2O_3 + 3Pt = Pt_3Al + 3/2\ O_2 \quad \Delta H_2 = 170\ kcal$$
Equation 2

For Equation 1, ΔH amounts to an oxygen vapour pressure at 1200°C of $p_{O_2} \simeq 10^{-32}$, for Eqn. 2 of $p_{O_2} \simeq 10^{-22}$ torr making it possible to reduce Al_2O_3 with H_2 in the presence of platinum only. This example shows the decisive importance of the heat of decomposition of the oxides and of the heat of formation of the various intermetallic compounds for these reactions. From their results, Bronger and Klemm (6) concluded

that the heats of formation are highest for the platinum compounds and decrease on moving from platinum to palladium and from platinum via iridium to osmium. This makes ruthenium the metal least likely to react with base metal oxides in hydrogen.

A summary of the results of Bronger's hydrogen reduction experiments is given in the Table. In general an increase in the reaction temperature decreases the concentration of the noble metal in the intermetallic compound, as can be seen for platinum-aluminium alloys. With alumina, silica and titania the AB-phases RuSi, RhAl, PdAl, IrSi and IrAl were obtained, whereas in almost all other reactions only those phases containing more than 50 atomic per cent platinum metals were synthesised. The explanation may be that Al_2O_3, TiO_2 and SiO_2 have low heats of formation (-135.5, -112.5 and -105.0 kcals per mol of O_2).

From these results one must conclude that refractories based on lime, magnesia or the rare earths should be preferred to aluminous materials for use in contact with industrial platinum equipment where reducing conditions are likely to be encountered. The behaviour of thoria and zirconia under such conditions has, unfortunately, not yet been investigated. Since it is known that the affinity of platinum for thorium and zirconium is stronger than its desire for aluminium, (3, 11) it seems fair to assume that zirconia and thoria will also react readily with platinum in hydrogen.

Reactions in Carbon Monoxide

Carbon monoxide is often present in combustion gases and may therefore be of some danger to the platinum metals at the higher temperatures. Unlike hydrogen, carbon monoxide is insoluble in the platinum metals and, since no dilute solid solutions are involved, the reaction conditions are therefore likely to be somewhat simplified. A detailed study was undertaken at this Research Institute to establish the way in which the platinum metals reacted with base
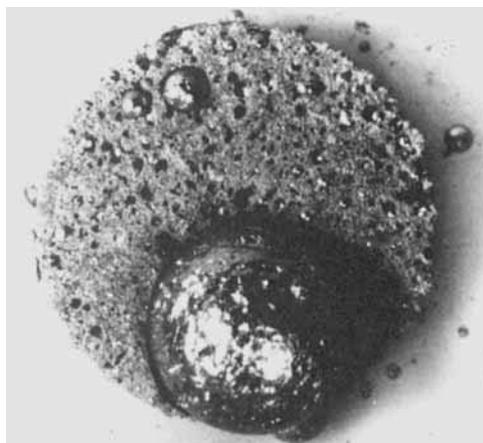
Fig. 1 Low melting point palladium-silicon eutectic on the surface of a palladium sample. Nominal composition 20 atomic per cent silicon, silicon added as silica, 1000°C, 100h, carbon monoxide atmosphere ×10 approx.
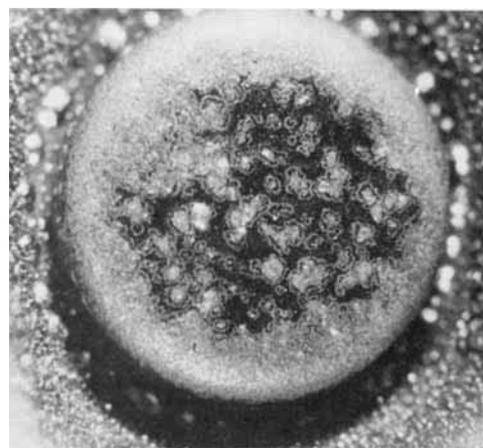
Fig. 2 Condensed palladium near the reaction pellet on an alumina substrate ×10 approx.

metal oxides, in a carbon monoxide atmosphere, at various temperatures, under practical conditions (12, 13).

At the temperature levels investigated, carbon monoxide was found to reduce the stable base metal oxides in contact with platinum in much the same way as hydrogen (12). Silica and zirconia reacted with palladium even below 1000°C, and above 800°C small molten droplets provided evidence of liquid phase formation, as shown in Figure 1. Figure 2 shows how palladium vapour,
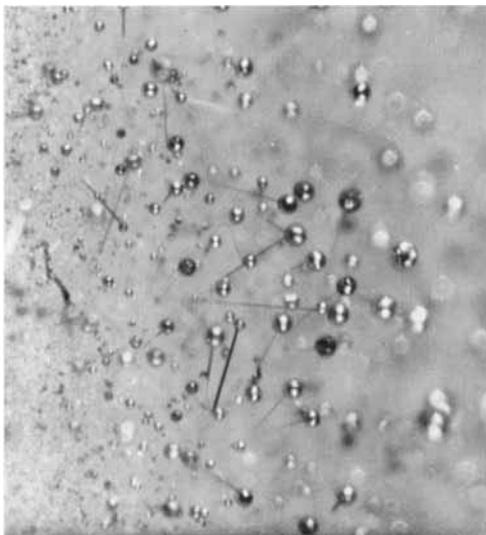
Fig. 3 Whiskers formed on the surface of a palladium sample. Nominal composition 20 atomic per cent magnesium, magnesium added as magnesia, 1400°C, 120h, carbon monoxide atmosphere ×45 approx.

formed above 1200°C, has reacted with the aluminous crucible material. Unusual whiskers were sometimes formed as a result of these reactions, those shown in Figure 3 being produced when palladium dissociated magnesia in the presence of carbon monoxide. Adorning the tip of each of these whiskers is a small ball having a duplex microstructure.

As in hydrogen, lime and magnesia reacted with the platinum metals under carbon monoxide less readily than silica and zirconia. The rare earth, Dy_2O_3 displayed remarkable resistance to decomposition, little evidence of reduction being seen even after 120 hours at 1400°C. When mixed with vanadium pentoxide, the platinum metals reacted quantitatively to produce f.c.c. solid solutions containing up to 40 atomic per cent vanadium.

Similarly quantitative reductions resulted from $Pd-Cr_2O_3$ and $Pd-TiO_2$ mixtures containing an excess of palladium. In other instances, for example, when palladium reacted with zirconium oxide, X-ray analysis indicated the presence of phases not delineated on the binary equilibrium diagram.

The diffraction patterns obtained contained many lines which were difficult to index. This complexity might be attributed to the presence of ternary carbides, or oxygen or carbon stabilised pseudo-binary compounds. The more or less continuous transition phases, such as those observed by Bronger et al. (6), which bridge the gap between one structure and another in the series $Pt-Pt_7Mg-Pt_3Mg$ might also be involved.
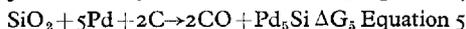
In carbon monoxide, as in hydrogen, platinum reacted strongly with the base metal oxides, being, in this respect at least as active as palladium. The hexagonal metals such as ruthenium were far more stable.

The reaction sintered pellets which resulted from these experiments sometimes displayed a fair amount of ductility even at high oxide concentrations, and it seems possible that technically viable methods of cermet production could be based on such reductions.

Reactions in the Presence of Carbon

These reactions, and especially their thermodynamics, have also been studied at this Research Institute, and some of the results obtained will be mentioned below.

When carbon is mixed with, for example, palladium and silica, the following reactions must be considered:

$$SiO_2 + 2C \rightarrow 2CO + Si \qquad \Delta G_3 \text{ Equation 3}$$
$$5Pd + Si \rightarrow Pd_5Si \qquad \Delta G_4 \text{ Equation 4}$$
$$SiO_2 + 5Pd + 2C \rightarrow 2CO + Pd_5Si \quad \Delta G_5 \text{ Equation 5}$$

For ΔG_5 we find
$$\Delta G_5 = \Delta G_4 + \Delta G_3 \qquad \text{Equation 6}$$
(ΔG = free enthalpy)

In addition the formation of carbides and solid solutions may add extra terms to Equation 6.

As has been mentioned earlier one of the decisive factors of the reaction is the free enthalpy of formation of the metallic phase (ΔG_4). If this is high the CO pressure above the cermet pellet will be increased, or at a constant CO pressure the reaction will occur at lower temperatures. We therefore studied the reactions by CO equilibrium pressure

Fig. 4 The dependence of the free energy ΔG of the f.c.c. palladium-chromium solid solution on the chromium concentration
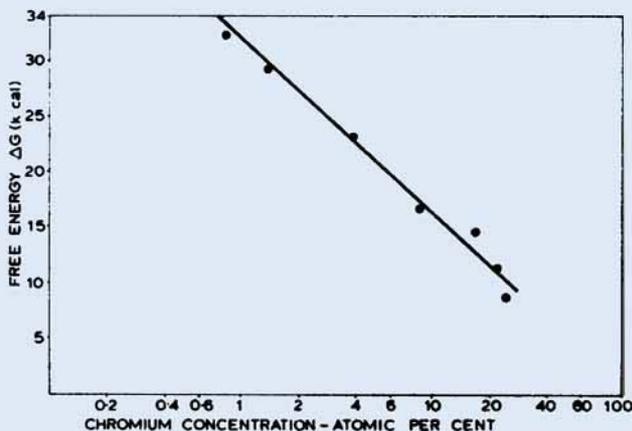
measurements, weight loss determinations and X-ray methods.

Chromic Oxide and Carbon

Although chromic oxide should theoretically be reduced by carbon at 600°C at pressures of 10^{-5} torr, practical tests showed no significant reaction until 800°C was reached. The presence of palladium strongly enhanced this reaction, a palladium-chromium solid solution being formed. At 900°C the carbide Cr_7C_3 was also detected.

Figure 4 shows how the free energy of formation of the solid solution (corresponding to ΔG_4 in Equation 6, the value of ΔG_3 for $Cr_2O_3 + 3C \rightarrow 2Cr + 3CO$ being taken from the literature) varies with the chromium concentration of the alloy which is formed. Platinum reacted with chromium less readily than palladium. Compared with palladium, rhodium had little influence on the reduction of chromic oxide with carbon. Ruthenium, however was more active. The reaction began at 700°C, and after 200 hours at 900°C the ruthenium solid solution which was formed contained 18 atomic per cent chromium.

Silica and Carbon in Vacuum

Both palladium and platinum have a similar influence on this reaction which begins at about 700°C. The palladium and platinum phases formed are, respectively, Pd_5Si, Pd_4Si, Pd_3Si; and Pt_3Si, Pt_7Si_3, Pt_2Si.

The formation of low melting point eutectics may complicate the reduction processes.

As shown in Figure 5, the partial molar free energy of formation of the Pd_xSi_y phases is not greatly influenced by the amount of silica reduced to silicon. The value of 30 kcals at 1000K might be attributable to the formation of Pd_3Si. With ruthenium a weak reaction starts at 900°C and at 1000°C small amounts of Ru_2Si can be detected by X-ray diffraction methods. Rhodium has no influence upon the reduction of silica with carbon up to 1000°C.

Zirconia and Carbon in Vacuum

Zirconia is readily reduced by carbon in the presence of platinum and palladium. As can be seen from Figure 5, the driving force for the reaction may be the high free energy of formation of Pd_3Zr. Over the temperature range investigated, the reaction ceased when the zirconium concentration in the reacted alloy exceeded 25 atomic per cent. Figure 6 shows how the surface reactions between the larger particles of zirconia, and the surrounding carbon and palladium powders, resulted in the formation of a reaction zone of Pd_3Zr which was deficient in carbon.

Magnesia and Carbon in Vacuum

Although the reactions with magnesia have not yet been fully clarified, it seems evident that the high weight losses which occur at
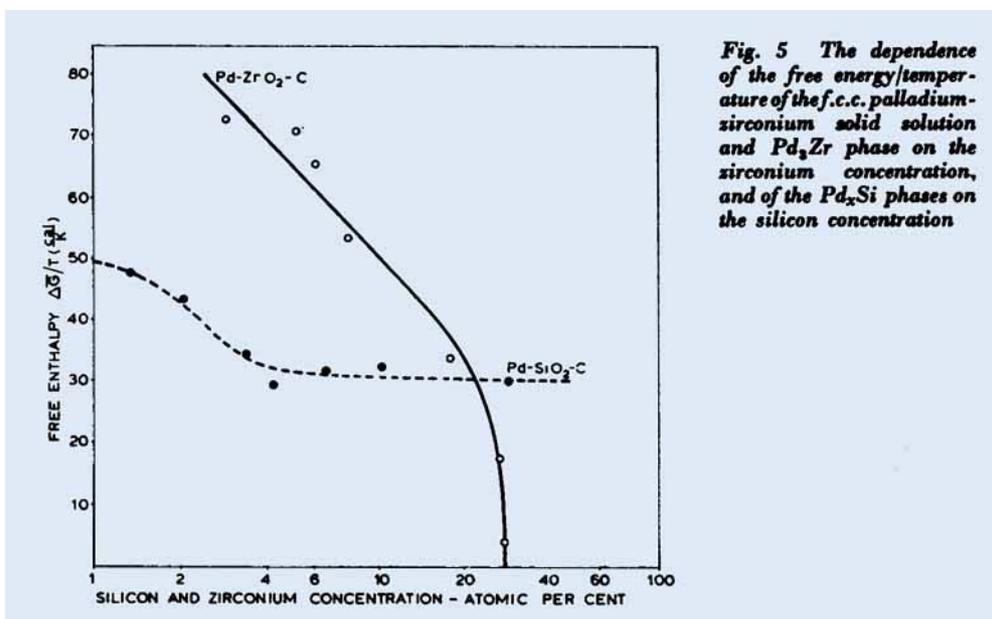
900°C can not be entirely attributed to the reduction of magnesia with carbon. Our experimental work shows that this occurs only at temperatures of 1100°C and above. Similarly, a mixture of palladium and magnesia shows little weight loss when heated, in the absence of carbon, up to 1100°C. The phases formed when magnesia is heated with both carbon and a platinum metal at 900°C and above are Pd$_3$Mg, Pt$_7$Mg and Pt$_3$Mg.

Above 1000°C, the weight losses which occur are unexpectedly high, and only traces of these intermetallic compounds can be detected. Similar effects are observed when magnesia is heated with carbon and ruthenium or rhodium. These effects might involve the formation of some volatile ternary phase, or the catalytic decomposition of the oxide which allows the magnesium to escape as vapour.

Reactions of Base Metal Oxides with Organic Vapours

Preliminary tests indicate that palladium-silica mixtures react readily at 900°C with propane and methyl alcohol. With platinum-silica mixtures the reaction proceeds rather slowly. A very low reaction rate is observed when mixtures of platinum or palladium are heated with zirconia or alumina in the above mentioned atmosphere.

Summary

The abilities of hydrogen, carbon, carbon monoxide and organic vapours to reduce the more stable refractory oxides are strongly
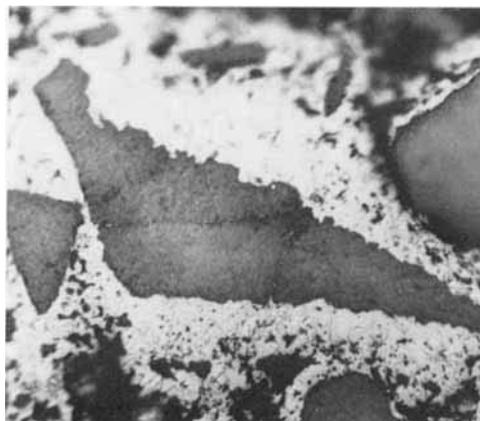
Fig. 6 A carbon-poor reaction zone around a zirconia particle. The zirconia surface has been corroded due to the formation of a palladium-zirconium alloy   *× 750 approx.*

enhanced by the presence of the platinum metals. Palladium and platinum tend, in general, to be more effective in promoting such reactions than ruthenium or rhodium.

Most of the reactions start in the temperature range 700 to 800°C, although reduction temperatures as low as 600°C have been observed. The driving force for these reactions is the high affinity of the platinum metals for the metal of the refractory oxide. This affinity results in the formation of intermetallic compounds or stable solid solutions, whose partial molar free energies of formation might be as high as −100 kcal per mol at 1000°C (the Pd/Pt-Mg systems).

The results of this experimental study are of value not only in helping to prevent damage to industrial platinum apparatus. They also suggest that metals could be brazed to refractory oxides with the aid of a platinum-containing brazing alloy, under suitably reducing conditions. Useful information on the thermodynamic behaviour of platinum metal alloys has also been obtained.

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High Temperature Thermodynamic Properties of Platinum-Titanium Alloys

Many of the enigmas of the interaction of platinum metal with other substances, in particular refractory oxides, are yielding to the systematic application of thermodynamic analysis, guided in no small measure by the Engel-Brewer predictions made over the past few years. Among the latest contributions to this field is the work recently reported by P. J. Meschter and W. L. Worrell (*Metall. Trans. A*, 1976, **7**, (2), 299–305) who describe high temperature thermodynamic measurements on platinum-titanium alloys.

The study concentrated on platinum-rich alloys containing 2 to 25 atomic per cent titanium and over the temperature range 1150 to 1400K. The thermodynamic information was obtained from e.m.f. measurements, using a solid ionic conductor as the electrolyte in a cell of the type:

$$NbO_2, Nb_2O_{4.8}/ThO_2(Y_2O_3)/\underline{Ti}(Pt), TiO_2$$
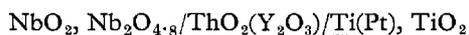
The e.m.f. data were used to derive the integral molar free energies, enthalpies and entropies for the range of platinum-titanium compositions studied, and also the partial molar quantities for platinum and titanium in the alloys. The activity of titanium in platinum was shown to be extremely low, that for the 20 per cent titanium alloy at 1300K being, $a_{Ti} = 2.6 \times 10^{-12}$. In accordance with Brewer's predictions, the standard free energies of formation of the intermetallic compounds also proved to be highly negative $\Delta G_f^\circ(TiPt_8) = -73.8$, and $\Delta G_f^\circ(TiPt_3) = -71.3$ kcal/g atom Ti at 1300K.

A tentative phase diagram is presented for the 0 to 25 atomic per cent titanium region of the system, based on the e.m.f. and X-ray data. It is proposed that $TiPt_8$ forms peritectoidally from $TiPt_3$ and Pt at 1350 ± 20K.

The authors have made similar thermodynamic studies of the related systems, Pt-Zr and Pt-Hf, and expect to present these in a future publication.   A. G. K.