Carbon in Platinum and Palladium

SOLUBILITY DETERMINATIONS AND DIFFUSION AT HIGH TEMPERATURES

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Carbon diffuses rapidly through heated membranes of platinum and palladium even though its solubility in the former metal is less than 0.02 per cent by weight at 1700°C. Palladium takes up more than 0.4 per cent by weight of carbon at 1400°C and this interstitial solubility hardens it considerably and distends the lattice. The effects of carbon on the microstructure and mechanical properties of platinum and palladium are described in this article, which dispels some illusions and surveys the practical consequences of the constitutional relationships observed.

Carbon depresses the melting points of all the platinum metals, and the eutectic temperatures and compositions have been determined by several investigators (1, 2, 3, 4). Although large quantities of carbon are dissolved in the molten state most of this is thrown out on solidification. Raub (3) considered that the eutectiferous structures of platinum- and palladium-carbon alloys were simple mechanical mixtures of the pure metals and carbon, and the solubility of carbon in solid platinum and palladium was reported as "vanishingly small". Very different results have recently been reported by Siller, Oates and McLellan (5), who concluded that both platinum and palladium take up substantial quantities of carbon after heating in contact with graphite powder for a few hours, at temperatures as low as 1200°C.

These workers did not examine the microstructure of their test specimens and assumed that all the carbon found was in the dissolved form. The use of silica heat-treatment capsules also introduced a considerable factor of uncertainty into their determinations.

The carbon-platinum and carbon-palladium alloys used in the present investigation were carefully studied by metallographic and X-ray diffraction techniques, and all treatments were carried out in platinum capsules, to avoid any possible siliceous contamination.

The platinum sponge and sheet used during this investigation for the manufacture of alloys by melting or solid state diffusion contained the following impurities:

Pd 0.003 per cent, Au 0.0001 per cent, Ca 0.0001 per cent, Fe 0.0005 per cent, Si <0.0001 per cent, Ag <0.0001 per cent.

A typical analysis obtained from the palladium sponge and sheet was as follows:

Pt 0.01 per cent, Rh 0.001 per cent, Au 0.0002 per cent, Al 0.001 per cent, Ca 0.001 per cent, Cu 0.001 per cent, Fe 0.002 per cent, Pb 0.0003 per cent, Ni 0.001 per cent, Si 0.0003 per cent, Ag 0.001 per cent.

The graphite crucibles and carbon powder employed contained not more than 5 parts per million of the spectrographically detectable elements. Carbon analyses on the binary alloys were carried out on 50 mg samples by a combustion-conductiometric method to an estimated accuracy at the 0.1 per cent level of ± 5 per cent.

Cast Duplex Alloys

As a first approach to this investigation 100 g batches of platinum or palladium sponge were melted in a high frequency
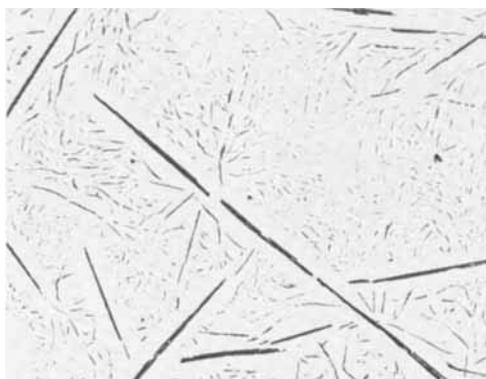
Fig. 1 Duplex carbon-platinum alloy produced by melting pure platinum in a graphite crucible. As cast. ×75
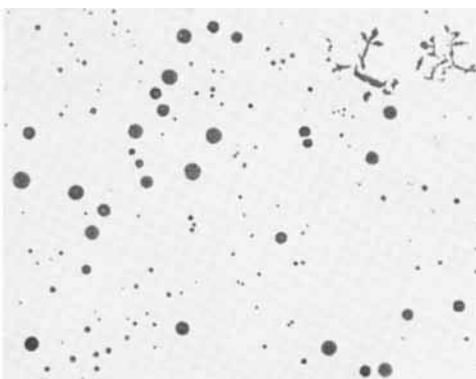

Fig. 2 Duplex carbon-palladium alloy produced by melting palladium on graphite. As cast. ×75

furnace in graphite crucibles. The charge was held molten for five minutes, following which the crucible, still containing the platinum metal, was quenched into water as rapidly as possible. Small slices of the quenched ingots were then reduced in thickness approximately 50 per cent by cold forging and solution treated at various temperatures for various times before being quenched into water. These heat treatments were carried out under a nitrogen atmosphere to avoid oxidation. Lattice parameters and micro-hardness determinations were made on carefully polished and etched microsections.

The duplex platinum-carbon alloys prepared by this method were not readily amenable to cold work and cracked quite severely under the forging hammer. The palladium alloys although considerably harder, were, by comparison, relatively ductile. Some typical microstructures are illustrated in Figs 1 and 2. The differing geometry of the primary graphite in the two metals provides a clear explanation for their differing response to cold work.

The lattice parameter of the platinum alloys changed little with quenching temperature whereas considerable expansion was
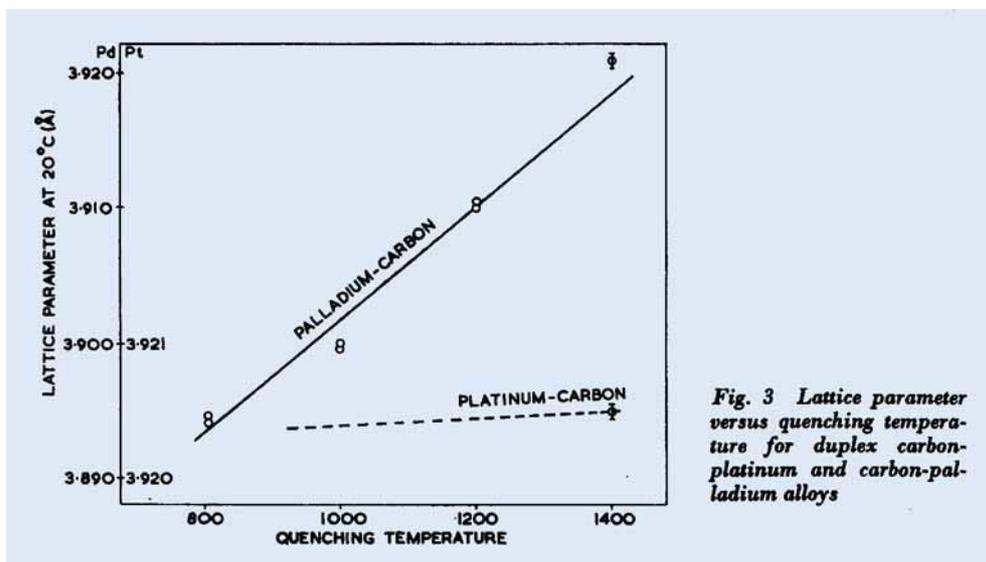

Fig. 3 Lattice parameter versus quenching temperature for duplex carbon-platinum and carbon-palladium alloys
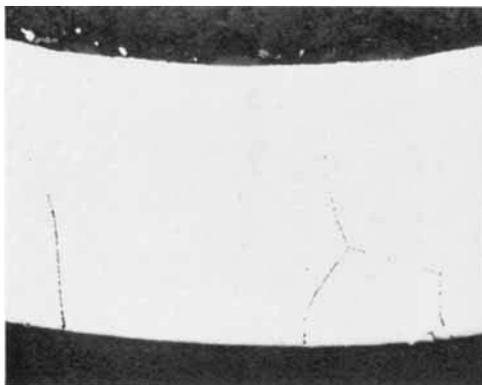
Fig. 4 Grain boundary porosity in the sheath of a platinum capsule containing graphite, heated in air for 75 hours at 1200°C. ×75.

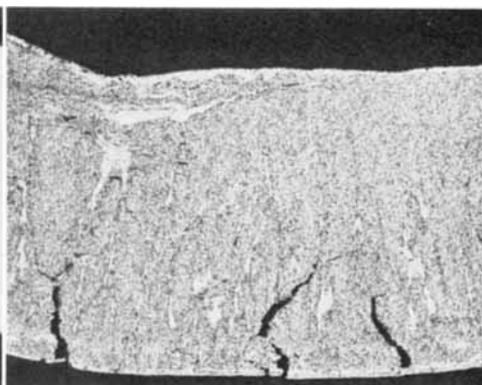Fig. 5 Porosity throughout the sheath of a palladium capsule containing graphite, heated in air for 18 hours at 1200°C. ×20

observed when the duplex alloys of palladium were quenched from high temperature. These results, plotted in Fig. 3, indicate that palladium dissolves measurable quantities of carbon, and platinum very little.

The slight changes in lattice parameter observed when carbon was equilibriated with platinum in this way could well be caused by the introduction of small quantities of dissolved impurity – usually of the order of 30 p.p.m. – during melting and casting.

Diffusion Experiments

To provide specimens containing smaller quantities of carbon than those which were readily obtained by melting and casting, sheets of platinum and palladium 0.020 inch thick were packed in high purity graphite

and sealed up in pure platinum capsules under a pressure less than 10^{-3} Torr. These capsules consisted of solid drawn platinum tubing having an internal diameter of 0.22 inch and a wall thickness of 0.020 inch.

For the purposes of the equilibrium studies, these capsules were normally heat-treated under an atmosphere of nitrogen. Some of the initial specimens were annealed in air and in these cases some unusual effects were observed. After 100 hours at 1400°C considerable surface distortion occurred and close examination revealed areas having a surface structure quite unlike that normally displayed by air annealed platinum. Similar effects were produced by burning carbon on the surfaces of a platinum sheet in air at 1400°C and it was concluded that the surface
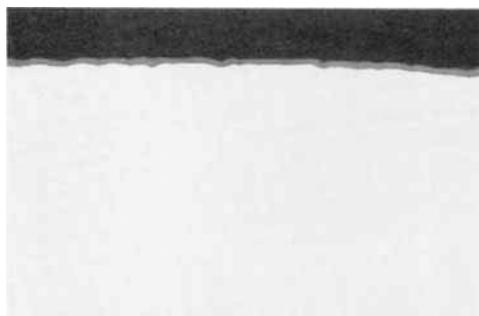

Fig. 6 Layer of graphite on the outer surface of a graphite-packed palladium capsule, heated in vacuo for 100 hours at 1200°C and slowly cooled. ×200
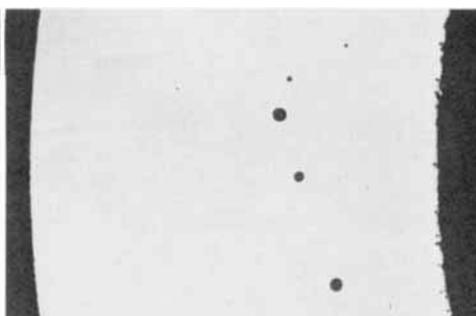
Fig. 7 Graphite spheroids precipitated towards the inner surface of the palladium sheath illustrated in Fig. 6. ×50

behaviour of the platinum capsules was caused by the combustion of carbon which must have diffused rapidly through the platinum membrane.

Micro-sections taken through these platinum capsules showed considerable grain boundary attack as shown in Fig. 4. Here the grains have opened up more than half way through the section of the tube. No attack of this sort was observed when empty platinum capsules were annealed in air, and the experimental observations are consistent with the view that carbon, although sparingly soluble in platinum, diffuses through it very rapidly at high temperatures when surface combustion produces the concentration gradients required. This localised intercrystalline attack was characteristic of the internal oxidation behaviour of platinum. Palladium capsules, when subjected to the same treatment showed uniformly distributed fine porosity throughout their cross-sections, as indicated in Fig. 5.

Both effects indicate a high rate of carbon diffusion. Oxygen is of course fairly soluble in the palladium lattice and this could account for the uniform porosity observed with the palladium capsules.

The lower solubility of oxygen in pure platinum probably confines the effect of the carbon/oxygen reaction to the grain boundaries.

In order to avoid the complicating effects of palladium oxidation some experiments were made on palladium tube capsules which, after packing with carbon, evacuating and sealing, were finally annealed *in vacuo* at 1400°C. These sealed capsules rapidly developed a black surface coating which was identified as pure carbon. The sections through such a palladium capsule shown in Figs 6 and 7 illustrate the thickness of this carbon sheath and also the spherulites of graphite precipitated out within the tube wall.

The volume of carbon present on the surface of the capsules was too great to be accounted for entirely in terms of the volatilisation of carbon saturated palladium *in*
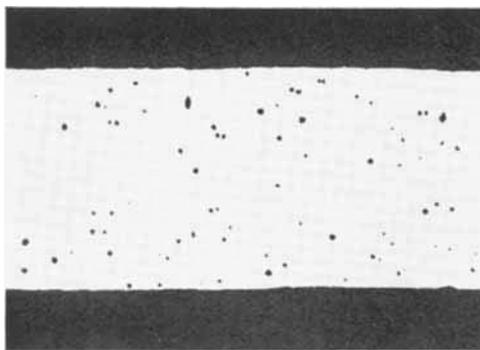

Fig. 8   Porosity in carbon saturated palladium sheet quenched from 1400°C.   ×75

vacuo. Fig. 7 shows that during the furnace cooling period following the annealing treatment graphite spherulites had precipitated out only within the inner half of the sheath section. It seems likely therefore, that the outer layer of graphite which formed initially as a consequence of surface volatilisation acted as a nucleation site for graphite attempting to separate from solid solution within the outer layers of the capsule during the slow cool. These carbon surface deposits were not observed on palladium capsules annealed
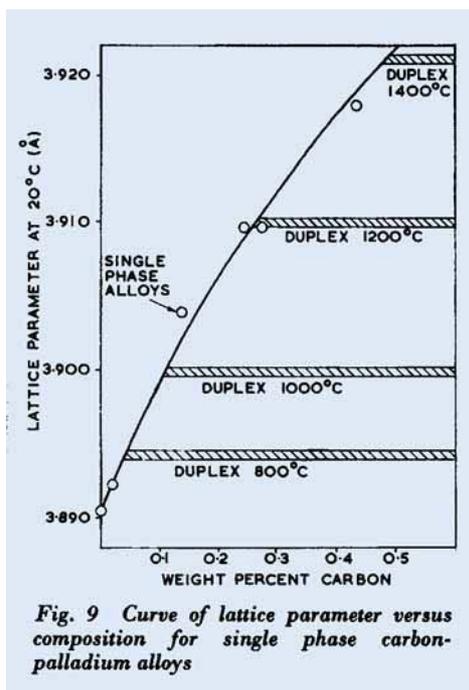

Fig. 9   Curve of lattice parameter versus composition for single phase carbon-palladium alloys
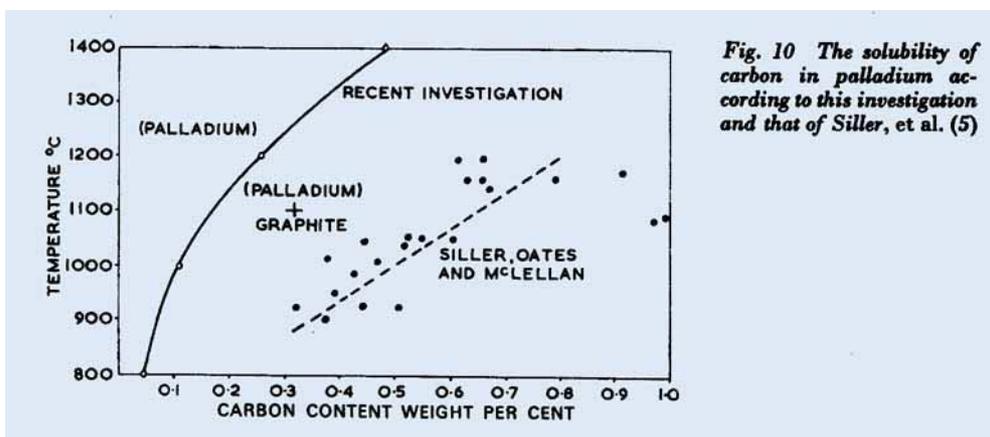
Fig. 10 The solubility of carbon in palladium according to this investigation and that of Siller, et al. (5)

in argon and rapidly quenched from the annealing temperature.

At this stage attempts were made to determine the rate of diffusion of carbon through platinum and palladium by heating sealed carbon containing capsules in air and measuring the change in weight. By carrying out blank runs on empty capsules the losses caused by carbon combustion could, it was hoped, be separated from those caused by oxidation and volatilisation of the platinum metal. These tests were, however, unsuccessful as capsule failure occurred long before the establishment of steady rates of weight loss.

Solubility Limits

Curves relating the lattice parameters and carbon contents of single phase alloys were required for accurate solubility determinations. The alloys needed were prepared by heating thin sheets of platinum and palladium in contact with carbon in sealed capsules as described above. The capsules were quenched in water after heat treatments ranging from 160 hours at 800°C to 7 hours at 1400°C. Half the sheet samples were analysed for carbon, the remainder being sectioned, polished and etched for microscopic and back reflection X-ray diffraction studies.

In the case of palladium, microhardness measurements provided a sensitive index of its carbon content, and to confirm the homo-geneity of the analytical specimens a series of hardness impressions were made across sections through the sheets which had been saturated with carbon by diffusion.

Palladium and platinum specimens saturated with carbon and quenched from 1400°C were porous as shown in Fig. 8. No porosity was detected in platinum or palladium quenched from 1200°C or below. No free or undissolved carbon or graphite was detected in any of the quenched specimens. The curve of lattice parameter versus carbon content in palladium is given in Fig. 9. Superimposed on this curve are the lattice parameters of the quenched duplex alloys, the solubility curve of carbon in palladium, shown in Fig. 10 being derived from this data.

Alloys quenched from temperatures above this line were simple solid solutions as shown by Fig. 11. Subsequent heat treatment at temperatures below the solubility line precipitated out carbon which at 800°C or below appeared as somewhat angular spheroids such as those shown in Fig. 12. These metallographic studies showed the true solubility of carbon in palladium to be much lower than the reported values of Siller, et al., whose results are plotted on Fig. 10 for purposes of comparison.

The absence of significant lattice parameter variations made it necessary to determine the solubility of carbon in platinum by microscopic methods. A number of synthetic

Fig. 11 *Palladium containing 0.25% of carbon in solid solution quenched from 1200°C.* ×75

Fig. 12 *Graphite spheroids precipitated from 0.25% carbon-palladium alloy by ageing at 800°C for 1 hour.* ×75

alloys was produced by melting in the argon arc furnace on a water cooled copper hearth. These alloys, containing from 1.5 to 0.004 per cent by weight of carbon, were carefully analysed after preparation. Sections from the ingots were heat treated *in vacuo* in a tantalum furnace and quenched after 7 hours at 1400°C or 5 hours at 1700°C. The carbon solubility appeared to be less than 0.02 per cent by weight at 1700°C. Small dark inclusions were observed in the 0.01 per cent carbon-platinum alloy quenched from 1400°C,

although it was difficult to ascertain, even at the highest optical magnification, whether these were particles of graphite, very fine porosity, or areas where graphite spheroids had been removed by polishing. These solubility values are well below those reported by Siller, *et al.*, which range up to 0.13 per cent by weight at 1245°C.

Hardness

Carbon increased considerably the hardness of palladium although it had little effect on platinum. The quenched hardness values for the palladium alloys are plotted on Fig. 13. The supersaturated solid solutions of carbon in palladium might well respond to age hardening treatments and considerable scope for further work exists in this direction.

Discussion and Possible Applications

These experimental results show that dissolved carbon has a considerable influence on the behaviour of both platinum and palladium. Although the solubility of carbon in platinum is very low, the rate of diffusion at high temperatures is exceedingly high. In some applications this must be regarded as a disappointment because the use of high modulus graphite fibres for platinum reinforcement has hitherto been considered an attractive possibility. The impracticability of this idea is unfortunately well illustrated
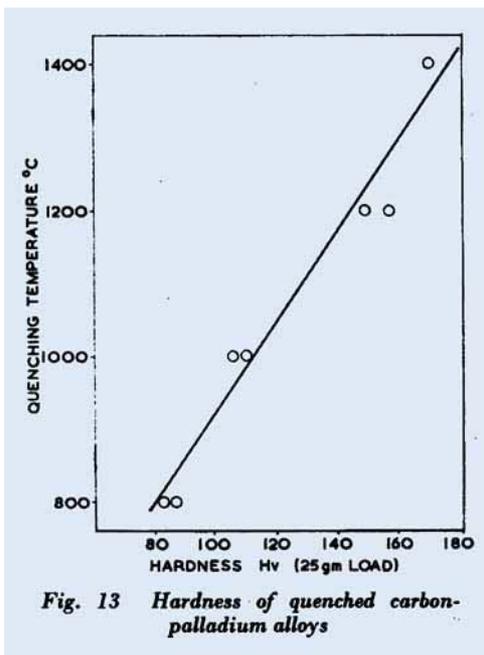

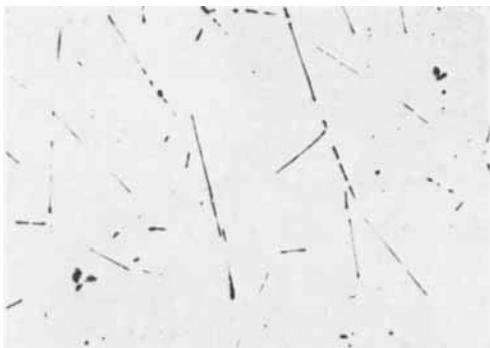Fig. 13 *Hardness of quenched carbon-palladium alloys*

Fig. 14 As cast carbon-platinum ingot after heating in air for 90 hours at 1400°C. ×75

by Fig. 14 which shows the cross-section of a duplex carbon-platinum alloy which has been annealed in air at 1400°C for 90 hours.

Before annealing, this specimen exhibited a microstructure comparable to that illustrated in Fig. 1. No graphite was observed in the section following the anneal in air, and the voids marking the outlines of the original primary graphite flakes were seen to break up and spheroidise as the heat treatment became more prolonged.

The prospects for carbon-palladium alloys are rather more attractive. The strengthening effects are considerable and it is possible that the precipitation of graphite from supersaturated palladium-based alloys could lead to the development of self-lubricating electrical slidewire resistances. It is not yet known whether the presence of dissolved carbon will accelerate or inhibit the diffusion of hydrogen through palladium. Since the solubility appears to be interstitial, further exploration in the low temperature regions of the solubility diagram might possibly reveal the existence of a miscibility gap similar to that observed in the hydrogen-palladium system. The greatly extended lattice parameter of these alloys might also influence the behaviour of palladium catalysts.

Accurate determinations of the rate of diffusion of carbon through platinum and palladium would indicate whether either of these metals could be seriously considered as a semi-permeable membrane for carbon.

Acknowledgements

References

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Spot Welding Platinum Foil on Titanium Anodes

Titanium anodes coated with platinum are used in many cathodic protection applications. Electrodeposited platinum is usually only a few micro-metres thick but for certain processes there is a platinum loss which calls for a layer of greater thickness. Hence, for example, platinum foil is used on the anodes that protect the drying cylinders of paper-making machines against the corrosive effect of the cooling sea water (1). For anodes used in this way, foil is cheaper per unit weight than electrodeposited platinum and the platinum loss is much less.

A. Baggerud of the Technical University of Norway reports (2) that spot welding of platinum foil to titanium has produced anodes which have protected drying cylinders successfully over several years. The method is reliable and no selective corrosion of the foil at the spot welds has occurred.

Baggerud has developed specifications for 30 and 50μm foils and tolerance limits for the welding current have been determined. Melting of the platinum foils must be minimised during welding lest magneto-hydrodynamic effects cause the formation of brittle intermetallic compounds. Oxides on the titanium surface have little effect on weldability and the Peltier effect is no real hindrance.

References

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