

Properties of Rhodium at High Temperatures

RESISTANCE TO CREEP AND CRYSTAL STRUCTURE DETERMINATIONS

Several years ago Dr Reinacher of Degussa found that the workability of rhodium could be greatly improved by bonding thin sheets of platinum to the exposed surfaces (1). He has recently compared the hot tensile strength and creep resistance of bare and platinum-sheathed rhodium with results (2) which cast considerable light on the reasons for the improved high temperature ductility.

The test specimens, in the form of 1.5 mm square rolled wire, were prepared with care. The rhodium tested at 1500°C was melted in high vacuum in lime crucibles and then cast into cylindrical ingots. These were rolled to square wire and platinum sheathed at an intermediate stage to produce a final sheathing thickness of 100 microns. The wires tested at 900°C and 1250°C were produced from rhodium which had been zone refined in a water-cooled platinum boat, and were given a 50 micron platinum sheathing. In both series of tests elongations were measured on a gauge length of 50 mm.

Hot Tensile Tests

Hot tensile testing was carried out in air on specimens previously annealed for one hour at 1400°C in hydrogen. Material tested at 250°C was considerably stronger than that tested at room temperature, and the high temperature tensile strengths did not fall below the room temperature values until 500°C was reached. Both the sheathed and unsheathed rhodium behaved in this manner, which suggests the operation of some form of strain-ageing mechanism. Worked rhodium has been shown to exhibit considerable hardness increases when annealed below 400°C (3)

and it is interesting to speculate on the migration of some gaseous impurity through the rhodium lattice to form atmospheres round dislocations. Rhodium can take significant quantities of oxygen into solid solution and it is perhaps significant that Dr Reinacher's careful preparation techniques did not specifically ensure the elimination of this impurity from his test pieces.

Platinum-sheathed rhodium had a lower tensile strength than bare material and this inferiority persisted up to 1500°C. Above 300°C, however, the sheathed wire gave consistently higher elongations, and this improvement in ductility was reflected in a greater tendency to neck before fracture.

Undue significance should not be ascribed to the numerical results of hot tensile testing which can rarely be justifiably compared with those of other investigators. The important feature of the tensile tests carried out by Dr Reinacher was that bare rhodium wire failed round the grain boundaries at all temperatures above 500°C, whereas platinum sheathing completely prevented this type of failure and ensured perfectly ductile fractures above 1000°C.

Creep Tests

Under creep conditions, however, the sheathed wire did not maintain this superiority. After a few hours at temperature all the platinum diffused into the rhodium and allowed considerable grain boundary cracking. At 1500°C the creep life of sheathed rhodium was no higher than that of bare wire.

The creep resistance and high temperature ductility of the platinum sheathed material

was found to be inferior to that of unsheathed rhodium tested by Douglass and Jaffee (4) in vacuum.

In view of Dr Reinacher's zone refinement techniques this inferiority cannot be attributed to the presence of metallic impurities. The plotted test results of the unsheathed rhodium did, however, exhibit a ductility minimum which was most pronounced at 1100°C and which coincided almost exactly with that of 10 per cent rhodium-platinum alloys tested under similar conditions. It is not unreasonable to associate these two effects and to consider whether they can be simply explained in terms of oxygen penetration along the grain boundaries.

Some of the more important creep test results are summarised in the table, which includes for purposes of comparison data from Jaffee *et al* (4) and from Sadowski (5). At

1500°C sheathed rhodium is approximately twice as strong as 10 per cent rhodium-platinum, but this advantage diminishes at lower temperatures. At 900°C the sheathed rhodium is inferior to Sadowski's 5 per cent platinum-rhodium tested at 927°C and to Jaffee's bare rhodium tested in vacuum at 1000°C.

This research of Dr Reinacher's has shown that the problem of the intercrystalline failure of rhodium and of rhodium-platinum alloys cannot be solved by using platinum sheathing. Sheathed rhodium tested in air is very little stronger than the 30 per cent rhodium-platinum alloy which is very many times more ductile, and there appears, therefore, to be little justification for the use of alloys containing more than 40 per cent of rhodium for high temperature service under oxidising conditions.

Creep Test Results on Rhodium and Rhodium-Platinum Alloys					
Alloy	Temperature °C	Stress for instantaneous failure p.s.i.	Stress for 10-hour life p.s.i.	Stress for 100-hour life p.s.i.	Reference
Sheathed Rhodium	1500	3960	1710	810	2
30 per cent RhPt	1500	3960	1130	582	2
10 per cent RhPt	1500	2420	810	483	2
Sheathed Rhodium	1250	7800	3420	1850	2
10 per cent RhPt	1250	5960	2130	1080	2
Bare Rhodium (vacuum)	1250	12800	7100		4
Bare Rhodium (vacuum)	1000	17100	11300		4
5 per cent PtRh	927		11300	7820	5
Sheathed Rhodium	900	17100	9950	7820	2
10 per cent RhPt	900	17100	6380	3830	2

Lattice Parameter Determinations

Until very recently the true high temperature structure of rhodium has been rather uncertain. Lattice parameter determinations have conflicted (6, 7) and have certainly not been sufficiently accurate to refute completely Rudnitsky's claim (8) that an allotropic modification occurred at 1030°C. Any existing uncertainty has been finally resolved by a paper emanating from the Department of Metallurgy at Oxford (9). This describes the design of two high temperature cameras with which accurate lattice parameters have been determined up to the melting point of rhodium. The face-centred cubic structure was observed up to 1960°C and the measurements provided no evidence whatever to suggest an allotropic modification. The mean coefficient of thermal expansion of rhodium varied from 8.8×10^{-6} per °C between 23 and 200°C to 12.4×10^{-6} for the range 20–1950°C.

These determinations on rhodium were made under completely inert atmospheric conditions and gave values for the lattice spacing very much lower than some previously

reported. In view of the effect of dissolved oxygen on creep resistance, the possibility of oxygen contamination during X-ray work should not be neglected. It is conceivable, for example, that Bale's (6) determinations may have, in fact, been made on a dilute solution of oxygen in rhodium.

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Platinum in Hydrogen Peroxide Production

AN IMPROVED ELECTROLYTIC PROCESS

The production of hydrogen peroxide on a very large scale is generally considered to be most economically carried out by the oxidation/reduction of anthraquinone. Smaller scale manufacture, however, is still by the older electrochemical processes which make use of the exceptionally high resistance of platinum to anodic oxidation.

Dr Joseph Müller, of Degussa, Rheinfelden/Baden, has recently described modifications to the Weissensteiner process—originally developed in 1905—which have resulted in substantial reductions in current consumption and space requirements. It is now believed to be the most economical of the electrochemical processes in operation (*Chemie-Ing. Techn.*, 1963, **35**, (5), 389–392).

Pure sulphuric acid is electrolysed using high anodic current densities to form per-

sulphuric acid, which on hydrolysis forms hydrogen peroxide. The latter is distilled off. The anodes consist of silver wires sheathed with platinum 60 to 85 microns thick. Later modifications of these anodes employed a platinum wire 0.12 mm diameter, 10 metres long, welded on to a tantalum sheath 150 microns thick enclosing a 1.2 mm diameter silver wire. The silver core provides high conductivity for the electrode to enable a uniform potential to be used along its entire length. The tantalum sheath protects the silver core from attack by sulphuric acid and the platinum wire carries the current into the solution to be electrolysed.

Each anode operates at the centre of a narrow-bore tube of porous porcelain which acts as a diaphragm to separate the anode and cathode reactions. Most of the cells in operation have had lives exceeding ten years.