Rhodium-Platinum Alloys

A CRITICAL REVIEW OF THEIR CONSTITUTION AND PROPERTIES

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In the second part of this article, concluded from the April issue of 'Platinum Metals Review', the author deals with the creep properties of the rhodium-platinum alloys, their resistance to oxidation and corrosion, and finally with their applications in industry.

In conditions where time must be considered as a third dimension in stress-strain relationships, the mechanical properties of rhodium-platinum alloys assume particular significance.

The room temperature creep properties of the 5 and 10 per cent rhodium-platinum alloys have been compared with those of pure platinum by Reinacher (42, 43). The curves in Fig. 12 illustrate that a tensile stress of approximately 7 tons per sq. in. applied to a 10 per cent rhodium-platinum test piece for 1000 hours causes a permanent extension of approximately 0.2 per cent. With pure platinum a stress of only 4.9 tons per sq. in. is sufficient to cause the same extension.

High Temperature Properties

Grain size has a decisive effect on creep behaviour at higher temperatures. Atkinson and Furman (44) have shown that a 10 per cent rhodium alloy having a mean grain size of 0.0021 in. tested at 400 lb. per sq. in. extended twice as rapidly at 750°C as pure platinum having a mean grain size of 0.004 in. By annealing at a sufficiently high temperature the grain size of the rhodium-platinum alloy was increased so that its creep rate became less than that of pure platinum.

As the alloys are rarely employed as structural elements in industrial equipment, slight dimensional changes at high temperatures are not usually of primary importance. Valuable information deals with the processes leading to ultimate failure at stresses of a few pounds per sq. in. and temperatures close to 1500°C. In this region the information provided by conventional creep testing has proved of little value, and time-to-rupture tests have provided most of the data at present available. Short-term tests for periods up to 30 hours provided the data summarised in Fig. 13,

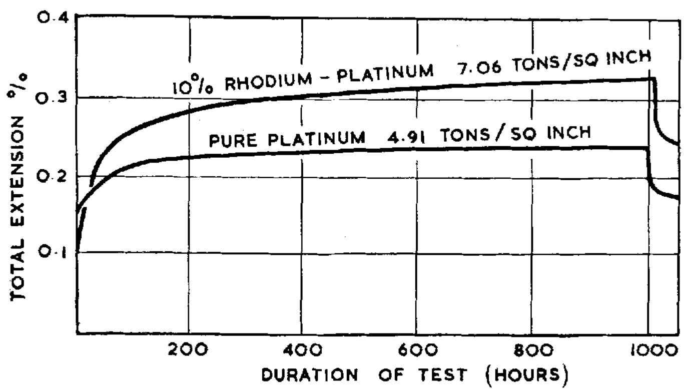

Fig. 12 Room temperature creep curves of pure platinum and of the 10 per cent rhodium-platinum alloy (Reference 42)

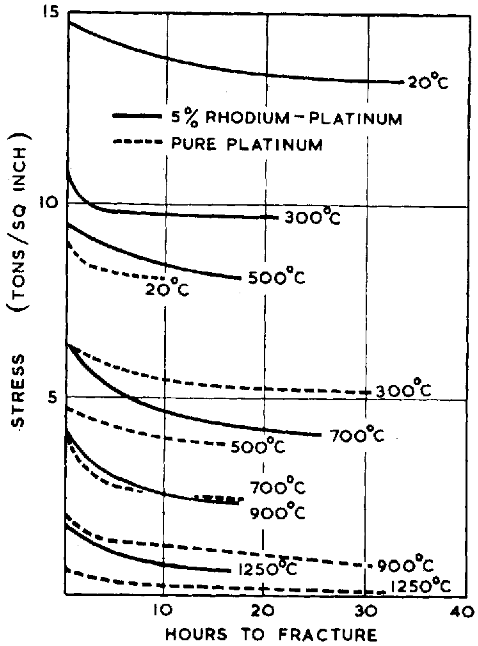

Fig. 13 Creep properties of pure platinum compared with those of the 5 per cent rhodium-platinum alloy at temperatures between 20 and 1250°C (Reference 43)

which compares the rupture properties of pure platinum with those of a 5 per cent rhodium-platinum alloy at temperatures between 20 and 1250°C (43). The table summarising the results of some long-term time-to-rupture tests at 900°C emphasises that rhodium additions as low as 0.5 per cent can improve considerably the room temperature properties of platinum (41).

The 0.5 per cent rhodium alloy resists fracture for considerably longer periods than pure platinum and has a much greater elongation. These results might appear to contradict data by Reinacher (43), who found that from 700° to 900°C rhodium alloys exhibited brittle fractures with considerable intercrystalline cracking, while pure platinum gave ductile fractures over this temperature range. Because Reinacher's tests were carried out at stress levels ten times higher than those tabulated above direct comparison of the results is not however justifiable.

Time-to-Rupture Tests at 900°C in Air				
Stress, tons per sq. in.	Pure Platinum		Platinum + 0.5 per cent Rhodium	
	Time to rupture, hours	Extension (per cent)	Time to rupture, hours	Extensions (per cent)
0.25	>1000	7		
0.50	92	12.5	665	91
0.75	22	14.0	99.0	63
1.00			33.0	92

Reinacher's findings agree with those of Stauss (45) that oxidation of the rhodium contributes to the brittle fracture of the alloys at high temperatures. Such effects were undoubtedly accentuated in Stauss's experiments, which were carried out on wires 0.010 inch diameter. Because creep is responsible for much high temperature thermocouple failure, stress-to-rupture tests on fine wires do, in this connection, afford valuable information. Experiments by Bennett (46) on wires 0.020 inch diameter stressed under oxidising conditions showed that at 1400°C the 10 per cent rhodium-platinum alloy was approximately eight times as strong as pure platinum, but that increasing the rhodium content above 20 per cent had little effect on the resistance to creep. Stresses as low as 200 lb. per sq. in. were capable of causing rapid failure of pure platinum at 1400°C, while the 13 per cent rhodium-platinum alloy could withstand approximately 1500 lb. per sq. in. for the same period.

Workability

By suitable hot forging processes all the rhodium-platinum alloys can be worked into rod, sheet or wire. Although the difficulty of working increases with rhodium content, pure rhodium can be readily forged at temperatures above 800°C. Swanger (47) of the National Bureau of Standards published details of working processes for the production of rhodium wire in 1929. He reported that the most forgeable metal was obtained by vacuum melting in fused thoria crucibles at pressures of the order of 0.5 to 1.0 mm Hg. The resultant product was then remelted in a hydrogen flame on a lime hearth.

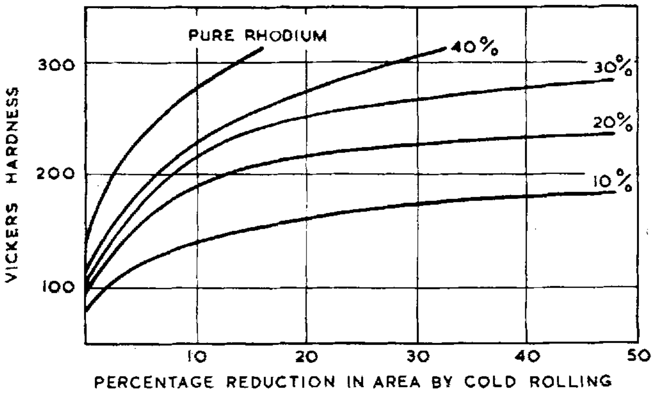

Fig. 14 Work hardening curves of rhodium-platinum alloys (Reference 41)

Argon arc melting is now preferred for alloys containing more than about 20 per cent of rhodium. The resultant ingot is hot forged at continually decreasing temperatures so that a fibrous structure is imparted to the product, which becomes progressively ductile until it can finally be worked at room temperature. Fig. 14 illustrates the effect of rhodium content on the rate of work hardening of cold rolled alloys (41). The rate of work hardening of rhodium is exceptionally high for a pure face-centred cubic metal. This subject has been discussed by Bale (20) and by Calverley and Rhys (48).

Oxidation and Corrosion Resistance

Rhodium additions reduce appreciably the volatilisation of pure platinum in oxygen at high temperatures. Raub and Plate (38) studied the changes in weight of alloys containing up to 40 per cent by weight of rhodium heated in a current of oxygen at atmospheric pressure to 900°C and 1100°C. Whereas pure platinum lost approximately 1 mg per sq. cm per 100 hours at 1100°C, the corresponding values for the 10, 20, 30 and 40 per cent rhodium alloys were 0.75, 0.70, 0.60 and 0.60 mg respectively. Alloys containing more than 30 per cent by weight of rhodium actually increased in weight when heated at 900°C, due to the formation of a fairly stable oxide. Although Wöhler and Muller (49) reported in 1925 the occurrence of Rh_2O, RhO and Rh_2O_3, modern thermodynamic evidence (50) suggests that Rh_2O_3, which has a corundum structure, is the only oxide stable over an appreciable temperature range. The dissociation temperature of Rh_2O_3 at 760 mm Hg oxygen pressure is 1115°C, a value in agreement with the data of Raub and Plate.

Alloys containing 20 to 30 per cent of rhodium develop a bluish oxide film fairly rapidly when heated to about 900°C in air. At higher temperatures this film decomposes to leave a bright surface. Thin bluish films are occasionally seen on the 10 and 13 per cent rhodium alloys when slowly cooled. Conditions appear to be fairly critical as the effect is not readily reproduced (41).

Large-scale tests on platinum alloy boats used for glass melting showed that appreciable evaporation took place from the 10 per cent rhodium alloy at 1450°C (41). The well-defined crystalline deposit which condensed on colder parts of the furnace had virtually the same composition as the parent alloy, indicating that no preferential evaporation of either element occurred.

Alloys containing more than 20 per cent of rhodium are virtually immune to attack by aqua regia. The 10 per cent rhodium alloy is particularly resistant to attack by free wet chlorine such as that produced by the combustion of halogenated organic vapours. Its superiority to pure platinum in this respect has been described by Crouch and Stauss (51).

Applications

The 10 per cent rhodium alloy, which has a higher electrical resistance and lower temperature coefficient than pure platinum, is used in large quantities as a durable furnace winding. The rhodium content increases the melting point, lowers the rate of volatilisation and minimises the rate of attack by silicious materials. High temperature laboratory furnaces frequently utilise windings containing up to 40 per cent of rhodium. For the highest temperatures pure rhodium windings are occasionally employed, but slight increase in maximum operating temperature rarely justifies the expense of this winding material which, because of its lower resistance and high temperature coefficient, presents considerable electrical control problems.

In the glass industry, which utilises considerable quantities of rhodium-platinum for electrically heated glass furnaces and for the bushings used in glass fibre production, the high melting point and chemical inertness of the 10 per cent alloy have long been appreciated. Rhodium-platinum is wetted less readily than pure platinum by molten glass (52), a factor which facilitates the industrial handling of this material.

Glow plugs in aircraft gas turbines have to withstand the combined effects of high temperatures, thermal shock, mechanical stress and chemical attack. In these conditions very satisfactory results are obtained with the 10 per cent rhodium-platinum alloy.

The applications of rhodium-platinum alloys to thermoelectric pyrometry have already been described. In most of the classical fixed point determinations, however, constant volume gas thermometers were employed. Thermometer bulbs constructed from 10 per cent rhodium-platinum were generally found to be superior to those of iridium-platinum for very precise determinations (53).

Laboratory crucibles containing up to 5 per cent of rhodium are stronger and more resistant to chemical attack than those of pure platinum.

In the textile field, rhodium-platinum spinnerets have now largely been superseded by gold-platinum alloys.

Gauzes used for the catalytic oxidation of ammonia to nitric acid are usually manufactured from the 5 and 10 per cent alloys, which are mechanically stronger and have a higher catalytic activity than pure platinum. The Andrussow process for converting methane and ammonia to hydrocyanic acid operates at higher temperatures in the region of 900 to 1200°C. Although rhodium-platinum has the same conversion efficiency as pure platinum in this process, the 5 and 10 per cent rhodium alloys are invariably employed simply because of their superior high temperature properties. Holzmann (54) has described various methods for recovering the rhodium-platinum particles carried over from the catalyst gauges in ammonia oxidation plants.

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