The Search for Alternatives to Rhodium-Platinum Alloys

USEFUL BUT LIMITED PROPERTIES IN THE INTERMEDIATE TEMPERATURE RANGE

By A. S. Darling
Johnson Matthey & Co Limited

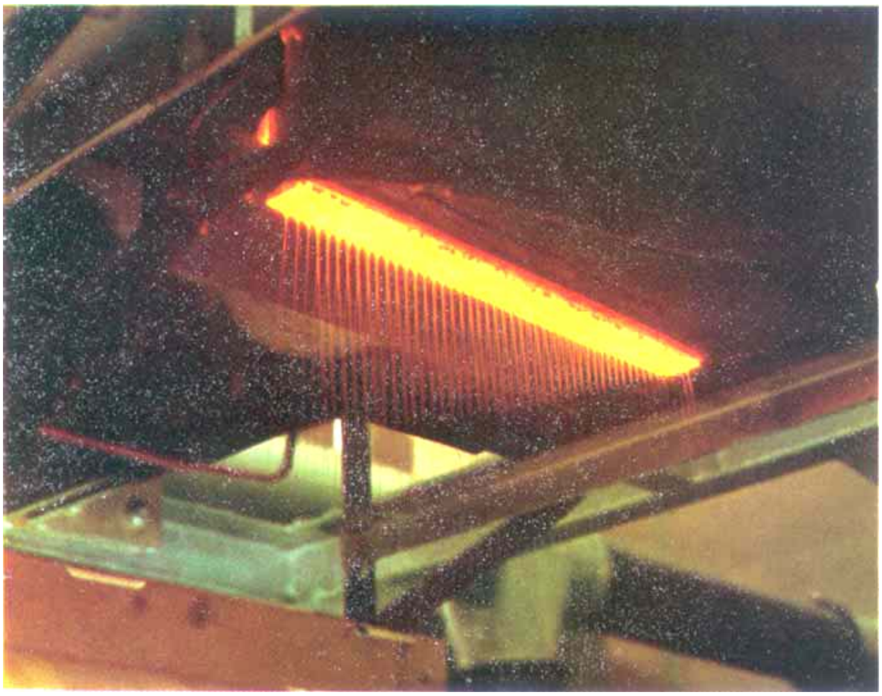
Extensive investigations of the high temperature strength and ductility of a number of platinum and palladium alloys have not yielded a successful replacement for the rhodium-platinum alloys so widely used in applications involving high stress, although they have indicated several alloys with economic possibilities at intermediate temperatures.

For many years rhodium-platinum alloys have been extensively employed for high temperature industrial applications, and in spite of their high initial cost no completely acceptable alternative has yet been evolved. At temperatures between 1000 and 1500°C platinum alloys containing from 10 up to 40 per cent of rhodium display satisfactory combinations of strength and ductility. The natural tendency of pure rhodium towards intercrystalline oxidation and failure at high temperatures is kept within manageable proportions by its platinum solvent, and these solid solution alloys are, moreover, very resistant to wetting by molten glass.

Attempts to reduce the intrinsic cost of the binary alloys by judicious additions of lighter or cheaper metals such as palladium and gold have, of course, been made but it was found that high temperature properties deteriorated rapidly when these metals were added in quantities sufficient to reduce appreciably the intrinsic cost of the alloy, and this conclusion, arrived at in the early 1950s, tended to discourage further efforts on these lines. During the last decade temperature levels in many industrial processes have been steadily rising, and a sizeable gap can now be seen between the maximum temperature levels at which nickel- and cobalt-base alloys can safely operate, and the more arduous region where temperature and stress conditions render the use of rhodium-platinum alloys absolutely essential. Cheaper and oxidation resistant alloys having useful mechanical properties in this intermediate range are therefore being currently sought.

Effect of Palladium on the Properties of Rhodium-Platinum Alloys

Palladium is cheaper and lighter than platinum, with a resistance to oxidation comparable to that of rhodium. Its value as a major additive to high temperature platinum alloys has therefore been carefully studied, particularly by Dr Gerhard Reinacher of Degussa. He concluded in 1958 (1), and confirmed in 1961 (2), that platinum alloyed with 4 per cent of palladium was more ductile than rhodium-platinum alloys between 700 and 1100°C. The results of an investigation published in 1962 (3) showed that 5 per cent of palladium could be safely added to a 5 per cent rhodium-platinum alloy without loss of high temperature strength and with a slight improvement in ductility at temperatures up to 1250°C. Palladium additions of 10 per cent had, however, an adverse effect upon both strength



One of the most exacting applications of rhodium-platinum alloys is in the production of fibre glass. The bushings, operating at around 1300°C, are highly stressed, and as yet no alternative material for their construction has been developed Photograph by Gullfiber AB

and ductility. Although the alloy containing 7 per cent of rhodium and 3 per cent of palladium had fairly good compromise properties, its strength and ductility at 1500°C were, however, very much inferior to those of the 10 per cent rhodium-platinum alloy. Furthermore, all the palladium-bearing alloys tested then exhibited intercrystalline cracking when creep tested at 900°C.

At this stage of development it seemed justifiable to conclude that any advantages resulting from the addition of palladium to rhodium-platinum alloys were not only marginal but apparent over a very limited temperature range. Outside this range the effects were detrimental, and the disadvantages involved appeared to preclude any industrial employment.

In the last two or three years, however, Dr Reinacher has set his sights on a somewhat different target in the hope of developing substantially lighter and cheaper alloys which, if not rivalling the high temperature performance of binary rhodium-platinum alloys, might still be justifiably employed under less stringent conditions. The technical characteristics of such materials must therefore be considered in relation to the economics resulting from their employment. In spite of its high cost per unit weight, rhodium can, on a volume basis, be freely interchanged with platinum, and because of its low density even slight reductions of intrinsic cost can be achieved with increase in rhodium content. Higher fabrication costs are likely, of course, to offset such intrinsic savings.

Substantial economies result, however, only by adding major quantities of palladium. The addition of 40 per cent of palladium, at the expense of platinum, to the 10 per cent rhodium-platinum alloy would reduce the intrinsic cost of the alloy by something like two-fifths. Such cost re-

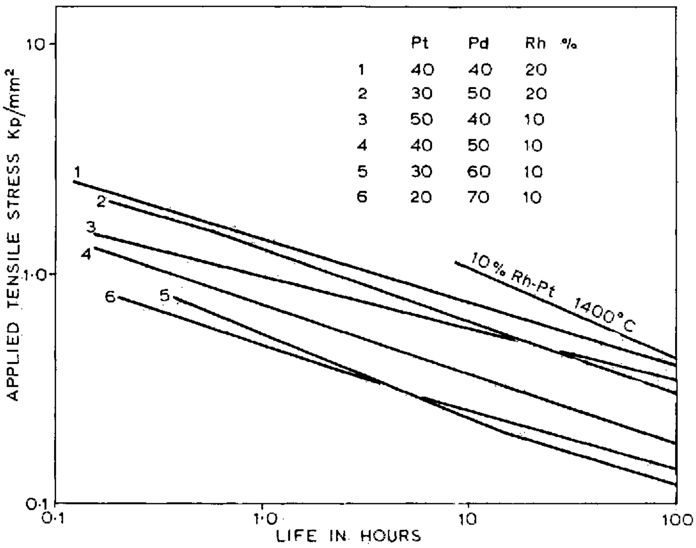


Fig. 1 Stress/rupture data on platinum-rhodium-palladium alloys creep tested in air at 1400°C. After Reinacher (4)

ductions would only be realised, however, if the component manufactured from the cheaper alloy was employed in conditions where operating temperatures and stresses were so low that no increase in thickness was required to compensate for the use of an intrinsically weaker material.

The alloys most carefully tested by Dr Reinacher contained from 40 to 70 per cent by weight of palladium and up to 20 per cent of rhodium (4, 5). Fig. 1 illustrates the results of some stress/rupture tests made on these alloys in air at 1400°C. In the short term all the alloys were very much weaker than the 10 per cent rhodium alloy, which was taken as a standard material. Since the creep tests were discontinued after 100 hours it is, however, very difficult to conclude with any degree of certainty how the alloys would perform after several thousand hours at temperature, a time period which would correspond more realistically with industrial requirements.

A significant feature of these stress/rupture curves is the anomalously low stress/time slope of the palladium-containing alloys. Pure palladium exhibits this characteristic to an even greater extent, and the curve

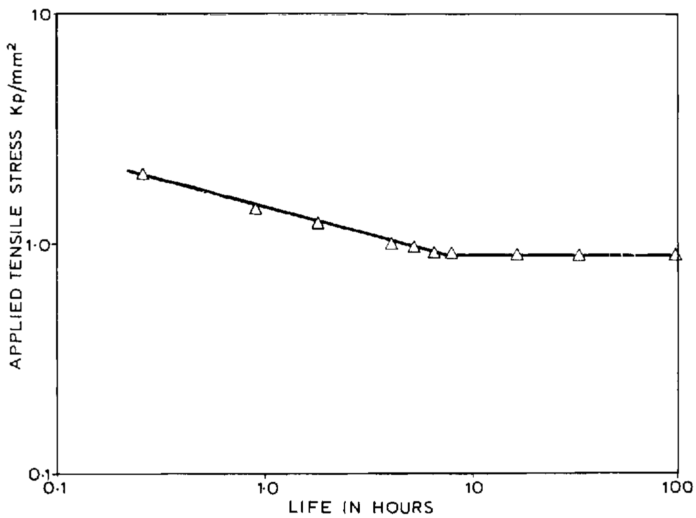


Fig. 2 Curve showing the effect of internal oxidation on the creep behaviour of pure palladium tested in air at 900°C. After Reinacher (6)

shown in Fig. 2, taken from Reinacher's 1962 paper (6) displays a pronounced inflexion after about nine hours at temperature, attributable to the internal oxidation of an oxygen permeable material. Dispersion strengthened materials display a similarly high sensitivity to applied stress, although in this instance the strengthening oxide dispersion is invariably one of high thermodynamic stability which will maintain its strengthening effect over long periods. The oxides responsible for temporarily strengthening the palladium alloys are those of any base metals which are fortuitously present as impurities. The oxide migration and agglomeration processes which inevitably occur, lead, therefore, after an initial strengthening régime to rapid cavitation, cracking and intercrystalline failure. Dr Reinacher's metallographic studies show that palladium-rhodium-platinum alloys exhibit, at high temperatures, many of the oxidation characteristics of pure palladium, although this tendency can be counteracted to some extent if the platinum content is sufficiently high. Thus, the Pt/Pd/Rh 20/70/10 alloy fails in an intercrystalline manner at 1400°C with little evidence of ductility, whereas the Pt/Pd/Rh 50/40/10 alloy necks down at 1400°C almost like the 10 per cent rhodium-platinum alloy to provide a reduction in area of almost 60 per cent.

Although area reductions are not always a reliable index of high temperature behaviour it is of interest to compare the values obtained on these palladium containing alloys with those yielded by the standard 10 per cent rhodium-platinum alloy. In Fig. 3 we see a valley, deeper than that existing in the palladium-free alloy, which marks the transition between intercrystalline and transcrystalline failure in tensile creep. Dangerously low ductilities are exhibited in this range by all the palladium alloys with the

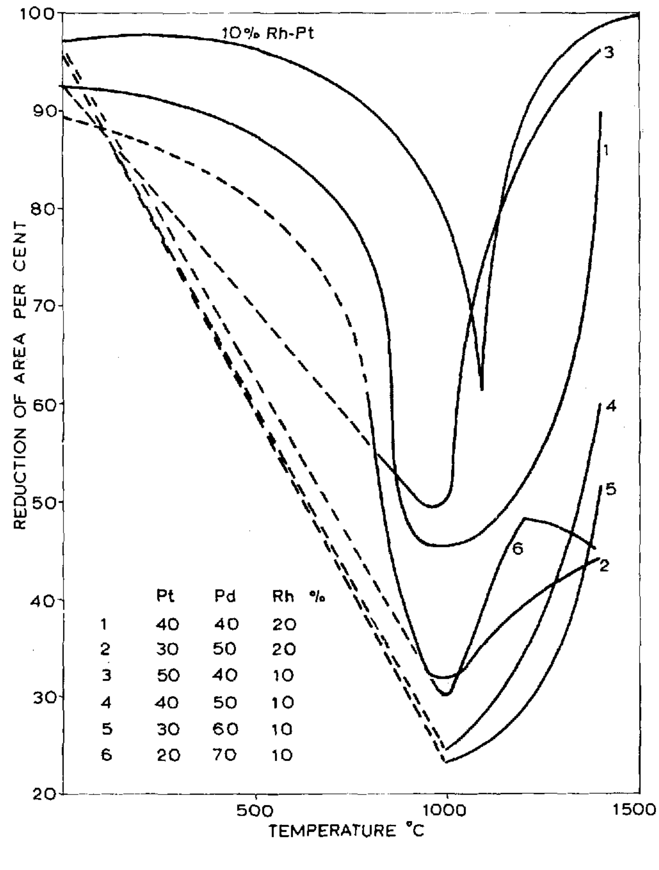


Fig. 3 Curves showing the serious fall in ductility which occurs in palladium-bearing rhodium-platinum alloys when tested in air in tension at temperatures around 1000°C. After Reinacher (4)

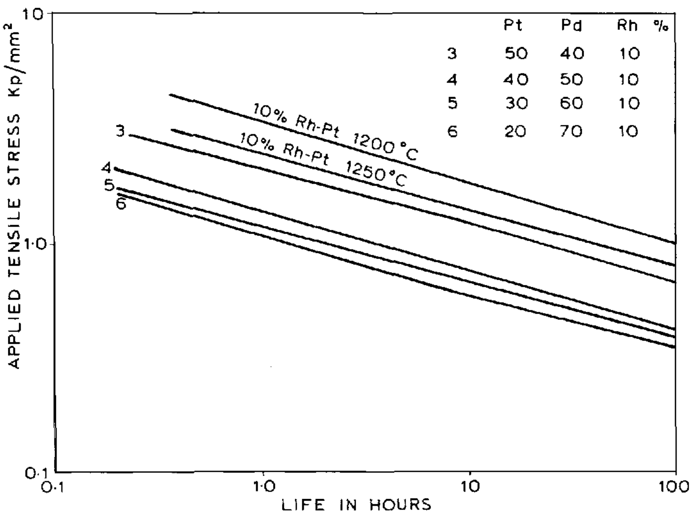


Fig. 4 Stress/rupture behaviour of platinum-rhodium-palladium alloys creep tested in air at 1200°C. After Reinacher (5)

exception of those containing 40 and 50 per cent of platinum, and the metallographic evidence provided in these papers shows that palladium contents higher than 50 per cent result in rapid intercrystalline failure even at temperatures as low as 1000°C.

The stress/rupture curves shown in Fig. 1, if extrapolated to longer periods, appeared to suggest that the Pt/Pd/Rh 50/40/10 alloy might possibly have characteristics which approached those of the 10 per cent rhodium-platinum alloy, and that its properties deserved further attention. Tests at 1200°C (5) confirmed the superiority of the 40 per cent palladium alloy over all the others which were examined, although at this temperature level its mechanical properties were well below those of the standard 10 per cent rhodium-platinum. Fig. 4 summarises the stress/rupture results obtained at 1200°C where the effects of oxidation were less pronounced than at 1400°C. The stress/rupture curves of the palladium alloys are all parallel with those of rhodium-platinum, and no anomalous intersections occur.

The alloy containing 50 per cent platinum is vastly superior to that which contains only 40 per cent of platinum, although it might be more accurate to ascribe the improvement to the corresponding reduction in palladium. For any given stress, however, the Pt/Pd/Rh 50/40/10 alloy tested at 1200°C appears to have a life only one-fifth that of the 10 per cent rhodium-platinum alloy tested at the same temperature. Even at 1250°C the binary rhodium-platinum alloy is still appreciably stronger than the palladium-bearing alloy at 1200°C.

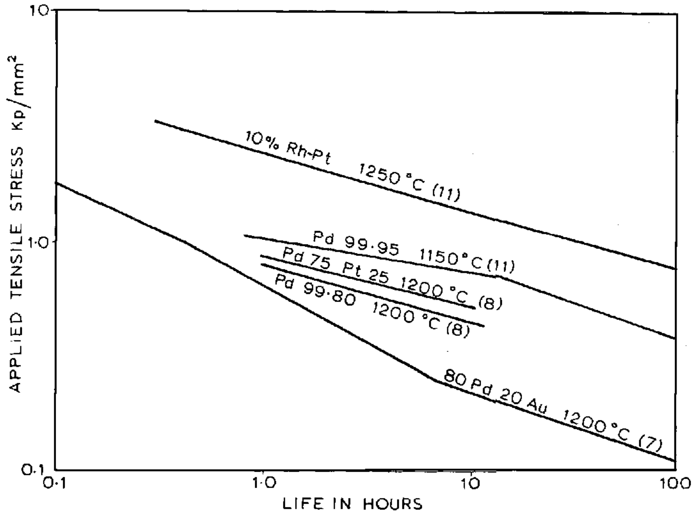
Properties of Palladium and Palladium-based Alloys

The resistance to high temperature creep of pure palladium is vastly inferior to that of pure platinum, as shown by the following data, also taken from (6).

Temperature °C	Palladium Stress for 100 hour Life kp/mm²	Platinum Stress for 100 hour Life kp/mm²
500	2.40	4.70
700	1.80	2.30
900	0.85	1.20
1100	0.29	0.51
1250	0.12	0.39

Some improvements in high-temperature behaviour can, however, be obtained by judicious alloying, particularly when the additions made are those which inhibit the

Fig. 5 Creep behaviour of palladium tested in air at 1200°C contrasted to that of gold-palladium and platinum-palladium alloys. The curves for palladium at 1150°C and for rhodium-platinum at 1250°C are inserted for purposes of comparison



natural oxidation tendencies of palladium. Surprisingly enough, although gold hinders oxidation to some extent, most gold-palladium alloys have a resistance to high temperature creep inferior to that of pure palladium. Fig. 5, based on data from Reinacher (7) and Rytvin (8), shows that, although the 80 Pd/20 Au alloy has a resistance to creep very much lower than that of pure palladium, the 25 Pt/75 Pd alloy is marginally better. Here again, however, the properties of the palladium alloys at 1200°C are well below those of the 10 per cent rhodium-platinum alloy at 1250°C.

The results of creep tests carried out for a few hours only do not provide a reasonable basis for extrapolation, and the high temperature properties and resistance to creep of palladium and its alloys obviously require more detailed study. In particular, the strength of palladium at high temperatures is greatly affected by its impurity content. Depending upon the base metals which are present, internal oxidation can produce grain boundary failure or dispersion strengthening, and discrepancies between the test results of Reinacher (6), Rytvin (8) and Sadowski (9) are probably attributable to this factor. Some of the defects inherent in pure palladium at high temperatures can, it is claimed, be reduced by small additions of iridium (10). Detailed studies have shown, however, (11) that the creep properties of the Ir/Pd 1.5/98.5 alloy are, at temperatures between 1150°C and 1400°C, much inferior to those of pure palladium, the iridium-palladium alloy extending in air at 1150°C approximately twenty times faster than pure palladium.

Although one might expect that the high rate of volatilisation of iridium under oxidising conditions at high temperatures would have an adverse effect upon the creep characteristics of any alloy of which it formed an integral part, this is apparently not always true. It has recently been suggested, for example (12), that oxide volatilisation can have a beneficial effect, and that by incorporating about 0.1 per cent of iridium into a rhodium-platinum alloy the high temperature characteristics of the latter will be greatly improved. In particular it is proposed that preferential oxidation and volatilisation of the iridium inhibits any oxidation of the basic rhodium-platinum alloy and thereby prevents deterioration during long service at high temperatures. It is also claimed that when the rhodium content of the alloy exceeds 40 per cent, small iridium additions improve strength, ductility and working characteristics.

This proposed use of iridium for sacrificial protection is certainly new and ingenious.

The alternatives to iridium suggested by the inventors are tungsten, rhenium, and molybdenum. Osmium has presumably been ruled out because of its high cost, although one is tempted to enquire how ruthenium would perform in a sacrificial role as its oxide is very much more volatile than that of iridium.

When considering the mechanisms involved in this proposed method of oxidation protection, it must also be borne in mind that the preferential volatilisation of iridium from iridium-rhodium alloys causes severe internal cavitation and rapid mechanical failure in air at temperatures around 1400°C.

Conclusions

The alloy containing 50 per cent of platinum, 40 per cent of palladium and 10 per cent of rhodium has high temperature properties which, although much below those of the 10 per cent rhodium-platinum alloy, are high enough to suggest that suitable applications might be found for it in the intermediate temperature range. Such materials, having an intrinsic metal cost about three-fifths that of the binary 10 per cent rhodium-platinum alloy, might possibly be used as substitute materials in lightly stressed components subjected to temperatures not exceeding something in the order of 1250°C.

As alloys for fibre glass bushings, where the rhodium-platinum alloys currently employed are already very highly stressed, the palladium-bearing alloys would be of little value, as the extra metal thicknesses required would offset any possible economic advantages.

High temperature platinum equipment must be welded and joined, and it would be of interest to hear how the welding properties of the palladium-bearing alloys compare with those of the more conventional materials. Excessive grain growth in and around fusion welds will almost certainly accentuate internal oxidation problems, particularly when the palladium content exceeds 20 per cent, and this is a subject deserving much closer attention. Pure palladium is very readily wetted by molten glasses in air, and it would therefore be of great interest to know whether the resistance to wetting of these palladium-bearing alloys is high enough to permit of their effective employment in glass handling operations.

Industry will use these new materials only if the resultant investment economies fully justify the solution of problems which will inevitably be caused by the substitution of a relatively untested and weaker material for the rather more expensive rhodium-platinum alloys whose characteristics are well known and understood. On this basis, therefore, a saving of two-fifths on the intrinsic metal cost, much of which will undoubtedly be swallowed up by increased fabrication and welding charges, might not provide a sufficiently powerful incentive for major changes in alloy usage. The maximum investment economies would obviously be realised if a really strong alloy containing at least 95 per cent of palladium could be developed. Such a material, which could have an intrinsic cost less than a third that of the rhodium-platinum alloy it might supplant, should find wide and profitable application at temperatures around 1250°C.

References

1 G. Reinacher, *Metall*, 1958, **12**, 622–628
2 G. Reinacher, *Metall*, 1961, **15**, 657–665
3 G. Reinacher, *Metall*, 1962, **16**, 662–668
4 G. Reinacher, *Metall*, 1971, **25**, 740–748
5 G. Reinacher, *Metall*, 1973, **27**, 659–661; see also *German Offen.* 1,950,468, April 1971
6 G. Reinacher, *Z. Metallkde.*, 1962, **53**, (7), 444–449
7 G. Reinacher, *Metall*, 1972, **26**, (7), 673–680
8 E. I. Rytvin, V. M. Kuz'min and A. E. Petrova, *Metalloved. Term. Obrabot. Metallov*, 1967, **2**, 31–32
9 E. P. Sadowski, "Refractory Metals and Alloys," Interscience Publishers, New York, London, 1961, p. 465
10 J. Aliotta, and E. L. Satterfield, *U.S. Patent* 3,488,172, Owens Corning
11 Johnson Matthey and Co Ltd, unpublished information
12 Owens Corning, *German Offen.* 2,154,517, May 1973