

Dispersion Strengthened Platinum

IMPROVED HIGH TEMPERATURE CREEP PROPERTIES

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Platinum containing small quantities of a dispersed carbide phase is stronger at high temperatures than many of the rhodium-platinum alloys produced by conventional techniques. It is stable under oxidising conditions and its valuable increments of strength are achieved without sacrificing any of the desirable characteristics traditionally associated with the use of platinum as a structural element. The physical and mechanical properties of this new material are described in this article and some possible applications briefly reviewed.

Because platinum is the only metallic structural material capable of operating for long periods under strongly oxidising conditions at high temperatures, it is important to consider how these attractive characteristics can be still further improved. The range of elements suitable for solid solution strengthening at high temperatures is very restricted indeed. Poor oxidation resistance rules out all the base metal transition elements, and within the platinum group itself osmium, ruthenium and iridium-platinum alloys are unsuitable for high temperature applications

because the oxides formed by these metals are extremely volatile. Severe surface erosion occurs in air and the intercrystalline failure caused by grain boundary oxygen penetration causes catastrophic failure after very short exposure to oxidation.

The natural tendency of pure rhodium to intercrystalline oxidation and failure at high temperatures can, however, be brought within manageable proportions by dilution. This, in essence, was the conclusion arrived at by Le Chatelier when he invented the 10 per cent rhodium-platinum: platinum thermocouple. It has since been established that the optimum creep properties of the rhodium-platinum solid solutions are exhibited by the alloy containing approximately 25 per cent by weight of rhodium.

The effect of composition on the ability of rhodium-platinum alloys to resist failure in air at high temperatures is illustrated by the curves in Fig. 1 (1, 2) which provide a good example of the law of diminishing returns so far as solid solution strengthening is concerned. Many experiments have shown that the prospects of obtaining, by alloying, high temperature properties superior to those of the 25 per cent rhodium-platinum alloy are rather limited. Ternary additions to the binary solid solutions have met with limited

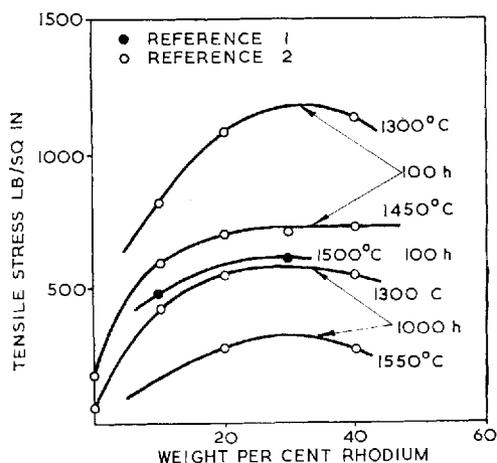


Fig. 1 Effect of composition on the ability of rhodium-platinum alloys to resist failure for periods of 100 and 1000 hours at high temperatures

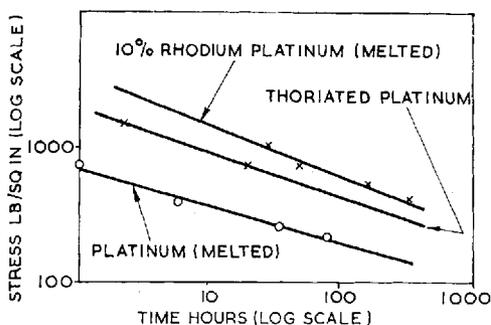


Fig. 2 Stress rupture data on thoriated platinum wires compared with those of pure platinum and rhodium-platinum wires produced by conventional methods

success, and it has been found that marginal improvements tend to disappear in air temperatures above 1250°C.

Considerations of this sort lead naturally, therefore, to the idea of platinum strengthened, not by alloying, but by a finely dispersed non-metallic phase.

Dispersed Phase Strengthening

General interest in the possibilities of dispersion strengthening was first aroused by the development of oxide-strengthened aluminium products such as SAP (3) which displayed remarkably high mechanical properties at temperatures approaching the melting point of aluminium. Subsequent work on dispersion strengthened copper and nickel has so far met with little commercial success largely because the mechanical properties of these materials become superior to those of conventional alloys only at temperature levels where catastrophic oxidation precludes their employment.

Platinum, however, being the only metal which is immune from these oxidation difficulties, becomes the logical candidate for dispersed phase strengthening and the results now being obtained suggest that considerable applications exist for this type of material.

Oxides, which when considered in isolation, appear to be the stablest type of compound have been extensively employed in dispersion strengthening studies. Thoriated platinum was introduced as long ago as 1942

(4) as a logical extrapolation of techniques well established in the lamp industry. As shown by the curves in Fig. 2 it provides pure platinum with a substantial increment of high temperature strength although the properties of conventionally produced rhodium-platinum alloys are not exceeded (5). Many other oxide dispersants for the strengthening of platinum have since been proposed (6).

Carbide Dispersants

Basic studies in the Johnson Matthey Research Laboratories showed several years ago that the free energy of formation of a compound provided little indication of what its stability would be when completely surrounded by a matrix of platinum. A rather surprising result of this investigation was the finding that carbides strengthened platinum more effectively than oxides (7) and that this strengthening effect could be achieved with concentrations of dispersant so low that the ductility, working characteristics and electrical properties of the platinum were not seriously impaired. This was a conclusion of great practical importance as some of the oxide strengthened platinum composites described in the literature contained up to 12 volume per cent of dispersant (8) and it seemed most unlikely that these cermet-like materials would satisfy many of the industrial requirements for platinum.

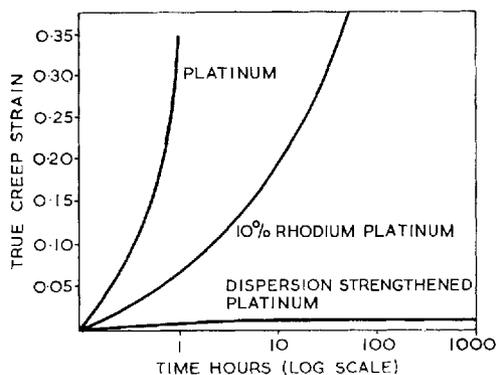


Fig. 3 Creep curve of dispersion strengthened platinum stabilised with a refractory carbide compared with those of pure platinum and 10 per cent rhodium-platinum produced by conventional methods. Temperature 1400°C, stress 750 lb/in²

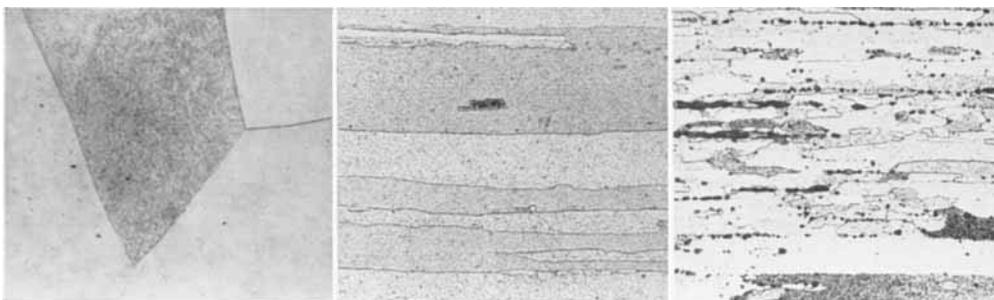


Fig. 4 This microstructure of a pure platinum wire after heating at 1400°C shows the very large grain structure developed in the material (×150)

Fig. 5 Microstructure of platinum wire with a titanium carbide dispersion which has recrystallised at 1400°C after being subjected to a 95 per cent reduction in area by cold drawing (×150)

Fig. 6 Platinum wire containing 0.2 per cent of thoria which has recrystallised at 1400°C after being subjected to a reduction in area of 95 per cent by cold drawing (×150)

Titanium carbide when dispersed in platinum to the extent of 0.04 to 0.08 per cent by weight was found to confer very interesting properties. Fig. 3 shows some typical creep curves obtained on $\frac{1}{8}$ inch diameter wires, tested in air at 1400°C. Under a tensile stress of 700 p.s.i. pure platinum wire obtained by drawing down a conventionally cast ingot endures for 30 to 60 minutes before failure. The life of the comparable 10 per cent rhodium-platinum wire, approximately 50 hours, is rather higher than that of the thoriated platinum wires produced from powder, whereas the carbide stabilised platinum wires last for about 1000 hours in the same stress and temperature conditions.

Discrepancies between the creep test results provided by sheet and wire specimens prompted a detailed microstructural examination of many dispersion strengthened platinum test pieces which had failed at high temperature. The vast majority of such failures, it was found, originated at grain boundaries, particularly those disposed transversely to the tensile stress axis. Although the reasons for this high temperature grain boundary weakness are still imperfectly understood, it was concluded that all transversely disposed boundaries should be regarded as potential sources of weakness, and a method was sought which would develop a grain structure having the lowest proportion

of grain boundary area in the direction most likely to be normal to the tensile stress axis.

Working and Recrystallisation Textures

Suitable grain structures were obtained by cold working and annealing procedures designed to produce highly developed recrystallisation textures (9). Platinum wires containing 0.04 per cent of titanium carbide, when subjected to a cold reduction of 95 per cent in area by drawing through a die, invariably recrystallised at 1400°C to produce a highly orientated grain structure in which only one-tenth to one-twentieth of the total boundary area was transversely disposed to the axis of the wire. Fig. 5 illustrates such a microstructure having highly elongated grains in which little evidence of a dispersed phase can be detected with the optical microscope. A correspondingly treated platinum wire containing 0.2 per cent of thoria is shown in Fig. 6. In spite of the higher proportion of dispersed phase this material has not developed such strong recrystallisation textures and the tendency of the thoria to agglomerate reflects itself in the inclusions present in the microstructure. Fig. 4 shows for comparison, the microstructure of pure platinum wire after similar treatment.

The effect upon the resultant creep properties of this working plus recrystallisation

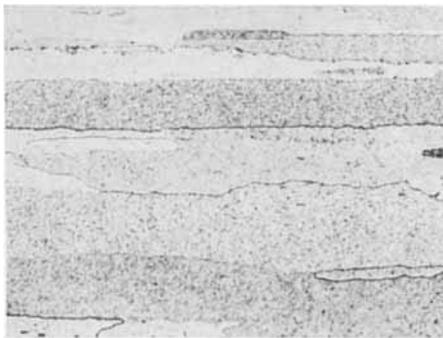


Fig. 7 Microstructure of sheet, recrystallised at 1400°C after the ingot from which it had been produced was cold swaged before cold rolling. The total reduction imposed by cold working was 90 per cent ($\times 150$)



Fig. 8 Microstructure of sheet, recrystallised at 1400°C after the ingot from which it had been produced was directly cold rolled. The total reduction imposed by cold working was 90 per cent ($\times 150$)

procedure can be observed from the test results given in Table I obtained from small powder metallurgy ingots containing 0.04 per cent of titanium carbide. After sintering for three hours at 1400°C these ingots were hot forged and finally reduced to sheet by cold rolling. The carefully machined sheet test pieces were stressed in tension at 1400°C in air.

Micro-examination of the sheet after creep testing showed a highly elongated grain structure in material from ingot 3, significant elongation in sheet from ingot 2 and a little if any elongation in sheet from ingot 1.

Processes such as swaging and wire drawing which deform the metal simultaneously in two directions are particularly effective in inducing those working textures which en-

courage the development of a highly aligned recrystallisation texture. Fig. 7 shows the pronounced recrystallisation texture of sheet from an ingot which has been cold swaged before rolling, the total cold reduction being 90 per cent in area. Although swaging and drawing are not appropriate working procedures in sheet production, flat cold rolling alone does not result in such an elongated grain structure when the sheet is finally annealed. As shown in Fig. 8, sheet which has merely been reduced 90 per cent in thickness by flat cold rolling recrystallises to produce grains, which, although elongated, are not so completely aligned as those of the partly swaged material. Although not so outstanding as those of wire the creep properties of dispersion strengthened platinum sheet, as shown in Table II, represent a very considerable improvement over those of conventionally produced 10 per cent rhodium-platinum sheet, being comparable to those of the alloy containing 25 per cent rhodium.

Dispersion Strengthened Alloys

Although dispersion strengthened pure platinum has mechanical properties superior to those of the rhodium-platinum alloys many applications can be envisaged where the alloy characteristics are necessary for reasons other than strength. Furnace windings provide a typical illustration, in which the electrical

Table I			
Ingot No.	Method of fabrication	Cold work total reduction per cent	Life in hours at 700 p.s.i. 1400°C
1	Directly cold rolled after hot forging	58	100
2	Directly cold rolled after hot forging	86	200
3	Ingot cold swaged before cold rolling	86	620

	Pure Pt, wire	Dispersion strengthened Pt, wire			Pure Pt, wire	Dispersion strengthened Pt, sheet	
Tensile stress, lb/in. ²	700	700	1400	2300	700	700	1400
Minimum life, hours	$\frac{1}{2}$ —1	1000	800	30	$\frac{1}{2}$	150	30

resistivity and low temperature coefficient of rhodium-platinum alloys are necessary for successful heating and current control although any improvement in strength at high temperature is obviously very valuable.

For this reason the dispersion strengthening technique has been applied to the 10 per cent rhodium-platinum alloys. As shown by the typical properties given in Table III, this material exhibits an outstandingly high resistance to creep.

Mechanical and Electrical Properties

Metals and alloys of this type, which contain only a small quantity of a dispersed phase, display greatly improved mechanical properties and resistance to creep with no significant change or sacrifice of the other properties. This valuable and important characteristic is illustrated by the physical properties given in Table IV. Although the dispersion strengthened materials commence to soften at much the same temperature as their conventionally produced counterparts they retain a much higher level of hardness to

much higher annealing temperatures and display a pronounced "hardness/temperature" plateau. The electrical properties of platinum containing small quantities of carbide are similar to those of pure platinum.

Applications

Where improved high temperature properties are required dispersion strengthened platinum or platinum alloys could offer considerable advantages over conventionally produced materials. In many instances they could be strong enough to be used in place of a more expensive rhodium alloy with consequent economy. In other applications dispersion strengthened platinum components could be run at higher temperatures with consequent savings in time and increased output.

Dispersion strengthened 10 per cent rhodium-platinum wire could function effectively as a furnace winding and reduce considerably the incidence of premature failure. Although high tensile stresses are not usually associated with the operation of resistance furnace elements appreciable creep occurs during heating and cooling because of the

	Conventional alloy			Dispersion strengthened alloy		
Tensile stress, lb/in. ²	700	1400	2300	700	1400	2300
Minimum life, hours	50	10	1	1000	1000	100

Table IV
Physical Properties of Dispersion Strengthened Platinum and a Rhodium-Platinum Alloy

	Melted Pt	Dispersion strengthened Pt	Melted 10% Rh-Pt	Dispersion strengthened 10% Rh-Pt
Specific gravity	21.4 gms/cc	21.288 gms/cc	20 gms/cc	19.862 gms/cc
Specific resistance at 20°C	10.6 $\mu\Omega\text{cm}$	12.0 $\mu\Omega\text{cm}$	18.4 $\mu\Omega\text{cm}$	21.22 $\mu\Omega\text{cm}$
Temperature coefficient 0-100°C	.00392 per °C	.0036 per °C	.0017 per °C	.0016 per °C
U.T.S. (annealed)	10 tons/in. ²	13.8 tons/in. ²	21 tons/in. ²	23 tons/in. ²
Elongation (annealed)	40%	35%	35%	30%
Modulus of elasticity (annealed)	22×10^6 lb/in. ²	23×10^6 lb/in. ²	27×10^6 lb/in. ²	28×10^6 lb/in. ²

differential thermal expansion between the winding and its refractory support. The electrical properties are so close to those of the conventional alloy that the improvement obtained with the dispersion strengthened wire in this application would be attributable to the high stability of the recrystallised grain structure and its increased mechanical strength at high temperatures.

Another possible application for dispersion strengthened 10 per cent rhodium-platinum is as the gauzes used for the oxidation of ammonia to nitric acid. There is no reason to suppose that the catalytic activity is not at least as high as that of gauzes made from the conventional melted and cast alloy. There are indications that less distortion occurs and that the rate of metal loss observed at about 850°C is lower than that of either pure platinum or 10 per cent rhodium-platinum, but this subject needs closer study.

The electrically heated wires used for igniting gas burners represent another application where catalytic activity and strength at high temperatures are required; promising results have been obtained with dispersion strengthened 10 per cent rhodium-platinum.

Although the pure platinum crucibles in which optical glass is currently melted yield a product of satisfactory quality they would

perform more effectively and economically if they were stronger at high temperature. Dispersion strengthened platinum offers the possibility of high temperature properties comparable to those of the higher rhodium-platinum alloys with no danger of glass discoloration. The extent to which these advantages can be utilised will depend upon the glass/metal wetting characteristics which are found to obtain and also on the availability of wide sheets of metal.

The applications so far described have been those in which the platinum works at a temperature level where its high strength can be attributed to the development of a well-defined recrystallisation texture. In this range the possible use of dispersion strengthened platinum for the manufacture of thermocouples and of resistance thermometer elements must also be considered although more work will be required before its suitability for such purposes can be properly assessed.

The welding and joining of dispersion strengthened platinum is a subject currently receiving a great deal of attention. Conventional fusion welding destroys the uniform array of fine carbide particles upon which the high temperature properties of this material depend, and any joints made in this way should be situated in the low-stress, low-

temperature regions of the apparatus involved where the mechanical demands imposed will be less severe. Alternative methods of joining such as resistance welding, electron beam welding and high temperature brazing are now being assessed on a laboratory basis.

During most of its working life high temperature platinum and rhodium-platinum apparatus of the normal type operates in the tertiary stages of creep and within such a context it is natural to expect and to tolerate considerable sagging and distortion. Dispersion strengthened platinum does not distort to the same extent. The linear elongations which occur before failure at 1400°C are usually about 1½ per cent and in

this respect dispersion strengthened platinum behaves like the more conventional materials of engineering construction.

References

- 1 G. Reinacher, *Metall*, 1963, 17, 699
- 2 H. Albert, D. Accinno and J. S. Hill, *Refractory Metals and Alloys*, New York, 1961, p. 465
- 3 R. Irmann, *Metallurgia*, 1952, 46, (275) 125
- 4 B.P. 578,956
- 5 Unpublished data, Johnson Matthey Research Laboratories
- 6 B.P. 645,681 645,682, 646,002, 646,003, 646,004, 645,541, 755,835
- 7 B.P. 830,628
- 8 A. S. Bufferd, K. M. Zwilsky, J. T. Blucher, N. J. Grant, *Internat. J. Powder Metall.*, 1967, 3, (1), 17-26
- 9 B.P. Application Nos 10239/64, 11886/64, 15973/64

Platinum in Austenitic Stainless Steel

The effects of adding 0.1 to 3.0 per cent of platinum to 18-12 austenitic stainless steel on the corrosion behaviour of the steel in superheated steam, normal sulphuric acid, and boiling magnesium chloride solutions have been studied in the course of a U.S./Euratom research and development programme carried out in Paris under the direction of Professor G. Chaudron (1).

Electropolished samples were maintained in an autoclave for 1000 hours in superheated steam at 500°C and 50 kg/cm² (710 lb/in.²). Addition of 3 per cent of platinum to a high purity steel containing 20 p.p.m. of carbon reduced the amount of oxide formation in these circumstances dramatically, the gain in weight being reduced from 122 to 9 mg/dm². In subsequent tests on an industrial vacuum-cast steel containing 90 to 100 p.p.m. of carbon, maintained for six days in superheated steam at 600°C and 70 kg/cm² (995 lb/in.²), the corrosion rate of 125 mg/dm was reduced about 20 per cent by the addition of 1 per cent of platinum.

The corrosion of platinum-containing stainless steels in sulphuric acid has been the subject of several studies in the past and the results of these are broadly confirmed by potentiokinetic observations here reported in air-free normal sulphuric acid at 25°C. The hydrogen overvoltage, although unaffected by the addition of 0.1 per cent of platinum to the steel, is considerably reduced by 1.0 per cent of platinum.

In these environments the increased corrosion resistance of the platinum-bearing steels is accompanied by changes in the character of the surface films. On commercial stainless steels, the films consist of two layers of nearly equal thickness, the outer one being crystallised and relatively soft and the inner being much more compact, harder, and more corrosion resistant. In steels of low carbon content, the inner layer becomes subject to intergranular oxidation, but platinum additions yield a thinner and perhaps tougher and more protective inner film, quite free from a tendency to intergranular oxidation.

In boiling magnesium chloride, the film formation due to platinum additions induces passivation (presumably reducing overall corrosion) but increases the tendency to stress corrosion (perhaps at grain-boundary discontinuities). In samples stressed at 35 kg/mm², the life was reduced from six hours to three hours by 0.1 per cent, and to one hour by 1.0 per cent of platinum.

It should perhaps be recorded that a brief note in the report disclaims the implication that the effects of platinum additions are confined to improving the protective nature of the surface films—the possibility that they may also improve the inherent corrosion resistance of austenite is not excluded.

J. C. C.

- 1 G. Chaudron, U.S./EURATOM R & D Program. Project No. 293. EURAEC Reports 1749 and 1804