Dispersion Strengthened Platinum

PROPERTIES AND CHARACTERISTICS OF A NEW HIGH TEMPERATURE MATERIAL

By G. L. Selman, J. G. Day and A. A. Bourne
Research Laboratories, Johnson Matthey & Co. Limited

Platinum can be strengthened very effectively for high temperature use by the addition of small quantities of a highly dispersed non-metallic phase, and recent work in the Johnson Matthey Research Laboratories has established processes which allow such a composite material to be produced consistently and reliably on an industrial scale. The new material, known commercially as ZGS platinum, is significantly stronger and more creep resistant than the conventional high temperature rhodium-platinum alloys, and yet retains the traditional characteristics which have given platinum its unique role in many industrial applications. This article describes the physical and mechanical properties of this dispersion strengthened product, highlights some of the areas in which it has been employed to advantage and discusses design factors in such uses.

Platinum has excelled as a material of construction for high temperature equipment in industry because of its unique chemical inertness. Its relatively low strength at elevated temperatures has been tolerated for this reason, and indeed compensated for quite effectively by the use of carefully designed refractory cradles or cores which support the loadings involved and ensure an economic life from the devices concerned. Nevertheless the basic lack of strength of platinum has imposed severe design limitations upon the user, and the need for a platinum-based material which is more resistant to creep deformation and failure at temperatures significantly above one half its absolute melting point has been recognised for many years. In certain applications it has been possible to consider alloying as a method of strengthening, and in the glass fibre industry, for example, rhodium-platinum alloys are employed with considerable advantage. The prospects of obtaining, by alloying, high temperature properties significantly superior to those of the 20 to 25 per cent rhodium-platinum compositions are rather limited, however, since further or alternative additions effectively destroy the ability of platinum to resist the degrading effects of prolonged high temperature use under oxidising conditions.

These limitations lead, of course, to the logical conclusion that the greatest advantages would be derived by incorporating within the platinum matrix a fine, well dispersed non-metallic phase, the benefits of which were discussed in a previous article in this journal (1). In spite of the attractions of this approach, however, and the great deal of effort expended on the development of a dispersion strengthened platinum, the problems associated with the need to achieve consistent and reproducible properties on a large scale have hitherto remained unsolved, and have prevented the establishment of a commercially viable product.

The Development of ZGS Platinum

In order to satisfy many of the industrial requirements for platinum, it is necessary to impose certain limitations upon the extent

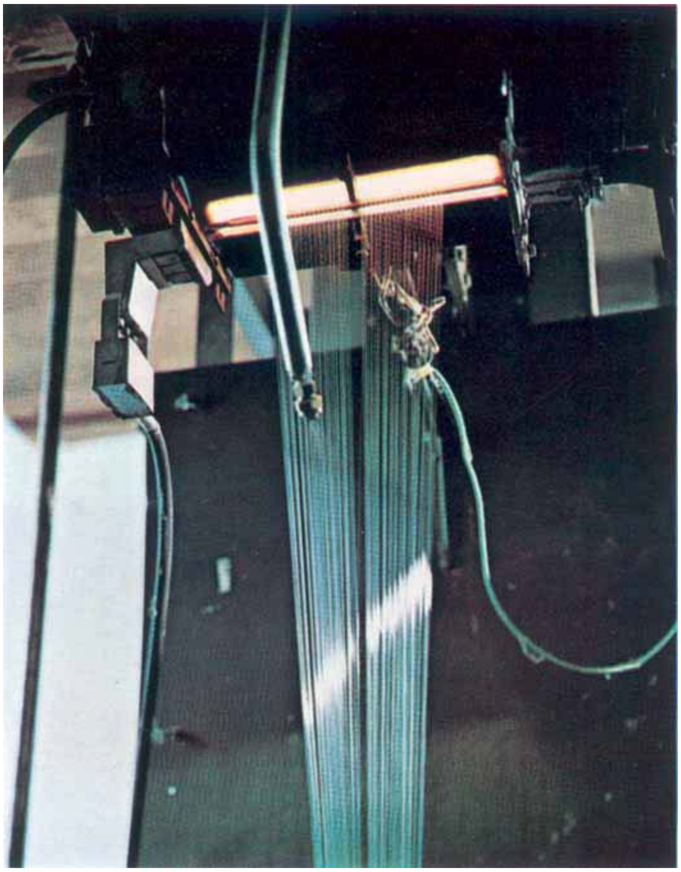


Fig. 1 One of the most exacting applications of platinum is in the production of fibre glass. This involves the rapid flow of molten glass at temperatures of 1250 to 1350°C through a series of orifices which must retain their size and alignment. Advances in production technique are demanding both larger bushings and higher operating temperatures at which the problem of distortion becomes more severe. Bushings incorporating the new dispersion hardened material, ZGS platinum, are in current production and are proving successful in overcoming these difficulties

to which dispersion strengthening is applied. High concentrations of dispersant can clearly provide a source of contamination in such impurity sensitive areas as optical glass production, and also impair the ductility and working characteristics as well as the electrical properties of platinum to an unacceptable degree.

In practical terms dispersant concentrations in excess of 0.5 volume per cent, corresponding roughly to an impurity concentration of 0.1 per cent by weight, are to be avoided. Such low levels leave very little margin for error during processing, and conventional manufacturing techniques – the blending together, for example, of platinum and oxide powders either directly or via intermediate compounds – cannot be controlled sufficiently well to guarantee the degree of dispersion required to give consistent properties in the final powder metallurgy product. This problem could be solved, however, if it were possible to form the dispersant in situ within the platinum matrix by an internal oxidation process similar to that applied quite successfully to metals such as copper and silver. In these cases a dilute alloy, silicon-copper for example, can be oxidised in such a way that the minor constituent reacts preferentially to form a fine oxide precipitate within the metal matrix.

Until recently the negligible solubility and diffusivity of oxygen in solid platinum was seen as a bar to an approach of this kind. Techniques have now been developed (2, 3), however, which effectively circumvent this problem, and allow for the formation of an extremely fine, uniformly spaced oxide precipitate by reaction between oxygen and platinum containing a small concentration of a reactive metal in solid or liquid solution.

This principle formed the basis for the development of a zirconia-strengthened platinum from a platinum alloy containing only 600 p.p.m. of zirconium metal in solid solution, which has extremely reproducible characteristics, and can be processed to sheet or wire in single batches up to 350 ounces in weight. This article describes the properties and characteristics of this new material, and provides some of the basic design data that the engineer will require for its application.

Room Temperature Properties

Some basic property data for ZGS platinum, pure platinum, and the 10 per cent rhodium-platinum alloy are presented in Table I. It is immediately apparent that the room temperature characteristics of platinum are little changed by the addition of a zirconia dispersant at the concentration employed. The electrical resistance is increased slightly, as expected, by the oxide addition, but the temperature coefficient of resistance is little affected. The low temperature mechanical properties of the dispersion strengthened product lie roughly midway between those of pure platinum and 10 per cent rhodium-platinum, and as the work hardening curves presented in Fig. 2 demonstrate, ZGS platinum in sheet form is very much easier to fabricate than the conventional melted alloy. This is an extremely important

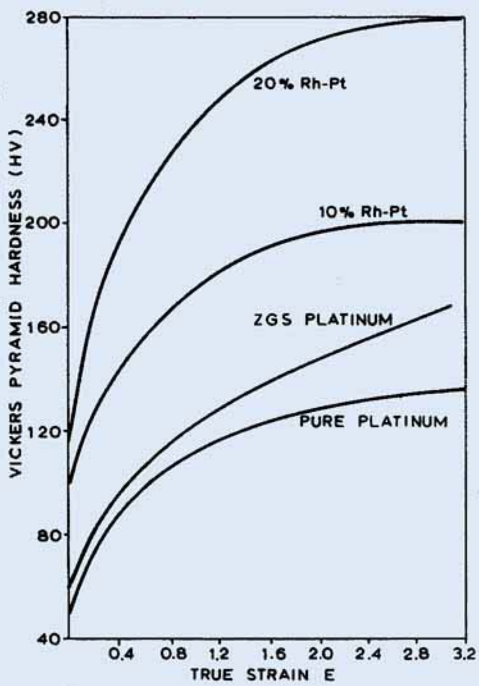


***Fig. 2** Work hardening characteristics of ZGS platinum compared to those of pure platinum and of rhodium-platinum alloys. These curves have been plotted on a basis of true strain* $E=\log_e\left(1+\frac{L-L_o}{L_o}\right)$*, where* L_o *and L are the original and final lengths*

Table I

Room Temperature Properties of ZGS Platinum, Pure Platinum and 10 per cent Rhodium-Platinum

	ZGS Pt	Melted Pt	Melted 10 per cent Rh-Pt
Specific gravity at 20°C, g/cm^3	21.38	21.45	20.00
Specific resistance at 20°C, μ ohm cm	11.12	10.6	18.4
Temperature coefficient of resistance per °C, Mean 0–100°C	0.0031	0.0039	0.0017
UTS, kg/mm^2 (annealed)	18.6	12.7	33.75
Elongation, % (annealed)	42	40	35
Hardness, H_v (annealed)	60	40.42	75

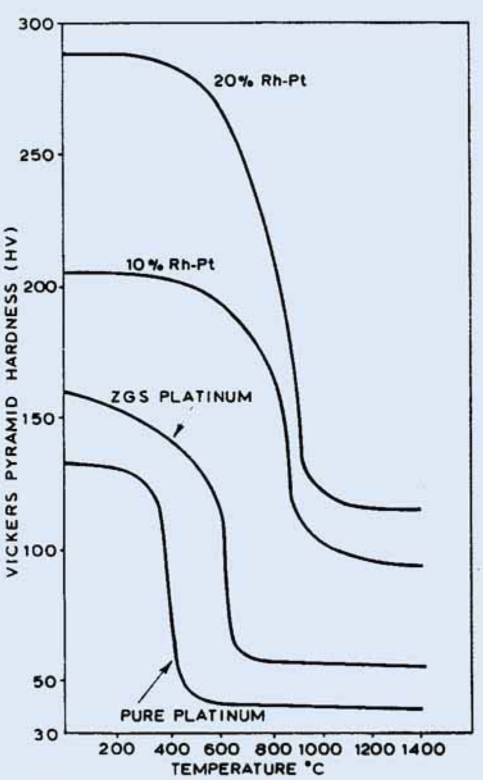


Fig. 3 Isochronal softening curves for ZGS platinum, pure platinum and two high temperature alloys. The hardness values were obtained on cold rolled sheet annealed for 30 min at the indicated temperature

characteristic within the context of equipment manufacture, in view of the general requirement to restrict or avoid the use of metal joining techniques during the assembly of ZGS components, a factor which will be considered in more detail in a subsequent section of this article.

Microstructure and Recrystallisation Behaviour

The low dispersoid concentration in ZGS platinum does not allow the development of the highly fibrous recrystallisation resistant microstructure which characterises many other dispersion strengthened products. Softening proceeds quite rapidly, as shown by the curves of Fig. 3, and in order to optimise the high temperature performance of such a material it is very necessary to adopt working and annealing procedures that develop highly aligned, stable, recrystallisation textures (4).

The microstructures of ZGS platinum and pure platinum sheet, in the as-recrystallised condition, are illustrated in Fig. 4. Fully recrystallised ZGS platinum has an exceptionally clean microstructure, and the oxide dispersion cannot be resolved under the optical microscope, being generally in the 200 to 1,000Å range. The individual grains are plate-like, and exhibit a high aspect ratio in sections both parallel and transverse to the rolling direction. The increments of strength derived from such a favourable microstructure operating in the creep regime are found to be virtually independent of specimen orientation. The high stability of the ZGS microstructure, compared to that of pure platinum is well illustrated by the photomicrographs of Fig. 5 which contrast the effect upon the two

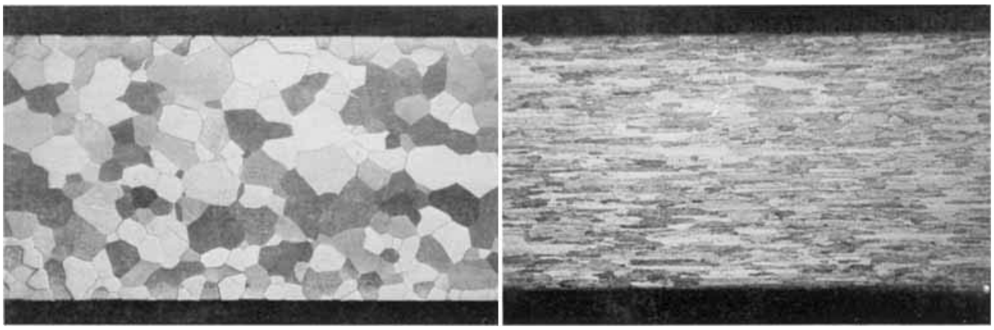


Fig. 4 The microstructures of pure platinum (left) and ZGS platinum sheet (right) after annealing for 30 min at 800°C and 1000°C respectively × 20

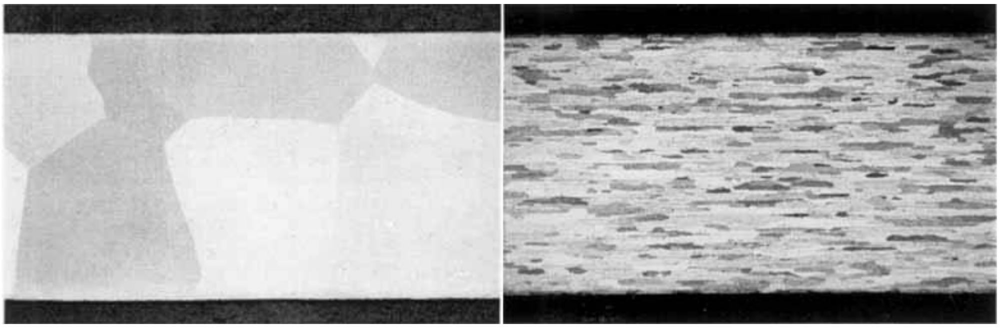


Fig. 5 The microstructures of pure platinum (left) and ZGS platinum sheet (right) after heating for 500 h at 1400°C in air. The high stability of the ZGS platinum microstructure during prolonged high temperature exposure is very apparent. × 20

materials of exposure for 500 hours at 1400°C in air.

Field experience has suggested that these highly aligned microstructures, which provide a very tortuous grain boundary path transverse to the sheet surface, exhibit an enhanced resistance to certain types of inter-granular contamination. This hitherto unsuspected effect has yet to be quantified in the laboratory, however.

High Temperature Properties

Platinum and rhodium-platinum alloys are normally employed in temperature and stress regimes where the predominant deformation process is grain boundary slide, enhanced in the case of alloys by diffusion effects (5), and it is under such conditions that the advantages of ZGS platinum become particularly apparent. The stress-rupture data presented in Fig. 6 were obtained from sheet specimens (1.5 mm thick), tested in air at 1400°C. At a stress of 1.0 kg/mm^2, well above that to which most industrial equipment would be subjected, ZGS endures for at least twice as long as the best alloy composition, and many times as long as pure platinum, before failure. The slopes of these stress-rupture plots indicate, as expected, that the endurance of the dispersion strenghtened product is more affected by increments of stress than its melted counterparts, and the performance of the former will be expected to improve, by comparison, at the lower stresses more typical of service conditions.

Stress rupture data for ZGS platinum over a range of temperatures from 1200 to 1500°C are plotted in Fig. 7.

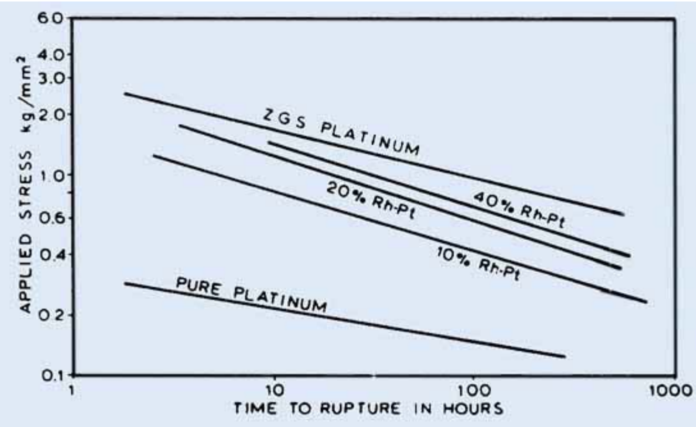


***Fig. 6** Stress/rupture properties of ZGS platinum compared to those of pure platinum and some commercially important rhodium-platinum alloys. These curves are based on tests made on 1.5 mm thick sheet specimens tested in air at 1400°C*

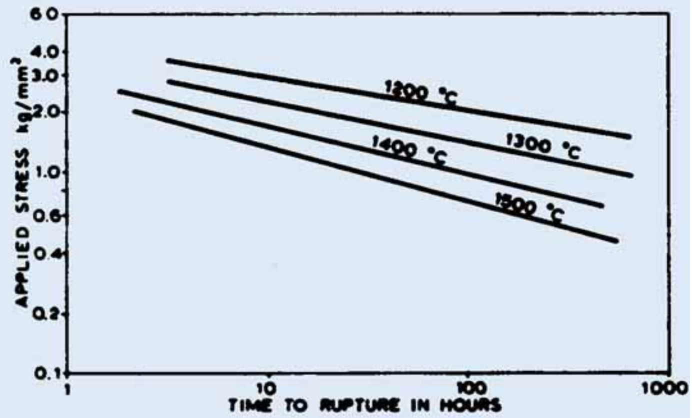


Fig. 7 Stress/rupture data for ZGS platinum sheet in the temperature range 1200–1500°C

While the stress rupture characteristics of the material are an important factor in the determination of design stress levels, it is probably true to say that in a majority of practical instances creep induced distortion has a greater influence on service life than material failure, unless the latter is prematurely occasioned by other factors such as contamination. Thus a glass-fibre bushing baseplate will generally be removed from service when creep has produced a degree of sag which is unacceptable in terms of efficient fibre production, and the requirement in this instance is for low levels of creep strain in the baseplate material.

The steady state creep rates of platinum, some rhodium-platinum alloys and ZGS platinum in sheet form are presented as a function of the applied stress at 1400°C in Fig. 8, and some typical values at this and other temperatures are tabulated in Table II. The high rigidity of ZGS platinum com-

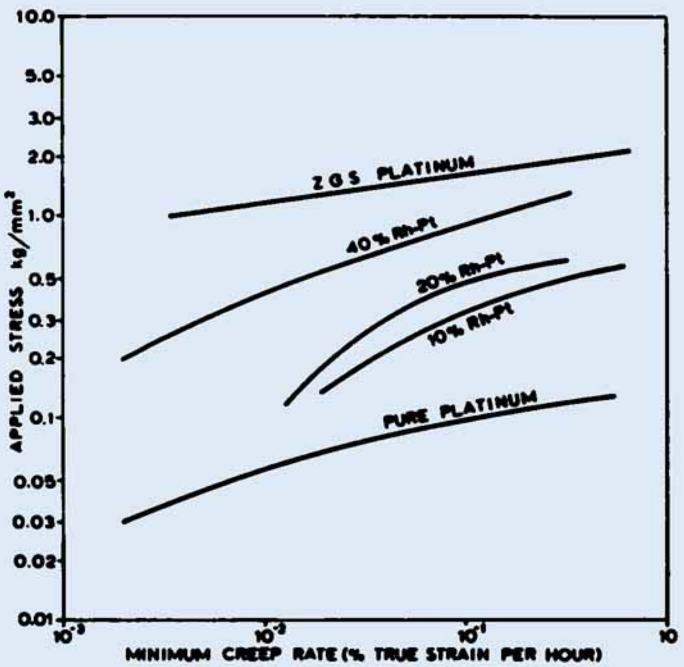


Fig. 8 Minimum creep rate curves for platinum, 10 per cent rhodium-platinum and ZGS platinum sheet tested in tension at 1400°C in air

Table II

Minimum Creep Rates of ZGS Platinum Sheet at Several Stresses and Temperatures (Per Cent True Strain per Hour)

Stress, kg/mm^2	1200°C	1300°C	1400°C
1.055	—	—	6.66×10^{-5}
1.406	—	1.65×10^{-4}	6.19×10^{-4}
1.758	2.66×10^{-5}	5.67×10^{-4}	2.8×10^{-3}
2.109	1.16×10^{-4}	2.21×10^{-3}	—
2.461	2.5×10^{-3}	1.39×10^{-2}	—

pared to the conventional melted products is readily appreciated from these results, which show, for example, that its creep rate at a stress of 1 kg/mm^2 (approximately 1400 lb/in^2) is almost two orders of magnitude lower than that of 40 per cent rhodium-platinum, the stiffest conventionally alloyed material. At lower levels of applied stress the strain rate plots for the melted alloy compositions are curved, an effect presumably associated with the greater contribution of diffusion processes during creep at low stresses in solid solutions of this kind (5). Under service conditions, therefore, an even more striking performance can be predicted from the dispersion strengthened product on the basis of these high stress short-term determinations.

At very high stresses, i.e. under conditions of very high strain rate, the resistance to deformation of ZGS platinum becomes very similar to that of the melted alloys. This effect is well illustrated by Table III, which details the results of hot tensile tests carried out on the various materials, with a cross-head speed of 1 mm/minute.

The hot tensile properties of ZGS platinum thus approximate to those of the 10 per cent rhodium-platinum alloy. This must be regarded as one of the most important characteristics of the new material, which has the capacity under service conditions to absorb the effect of shock loads and other transient stress concentrations without complete failure. It is imperative, however, that this basic property of ZGS platinum is taken fully into account when new applications are being considered. Situations have been encountered, for example, in which high temperature platinum apparatus develops gross distortions during service because of the extremely high transient stresses associated

Table III

Ultimate Tensile Strength of ZGS Platinum, Melted Platinum and Several Rhodium-Platinum Alloys at Room and Elevated Temperature

Test temperature	Tensile strength, kg/mm^2				
	Pure Pt	10% Rh-Pt	20% Rh-Pt	40% Rh-Pt	ZGS Pt
20°C annealed	12.7	33.75	48.8	57.5	18.6
1200°C	—	4.8	10.1	—	3.8
1400°C	<0.40	3.6	5.5	7.87	2.9
1500°C	—	—		—	2.4

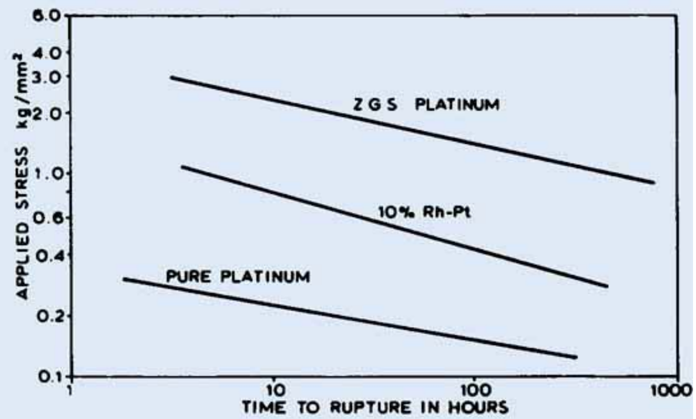


Fig. 9 Stress/rupture properties of ZGS platinum wire 1 mm diameter tested at 1400°C in air, compared with platinum and 10 per cent rhodium-platinum wires

with differential thermal expansion effects rather than long-term creep. In such instances the direct replacement of the conventional material of construction with ZGS platinum will not solve the problem. The constraints which allow the build up of very high stress levels during heating and/or cooling must be removed from the system by re-design before the benefits of the material change can be obtained.

Properties of ZGS Platinum Wire

The data presented in the previous sections of this article have referred exclusively to the performance of the new product in sheet form. While the major applications will undoubtedly consume sheet rather than wire, some data have been presented in Fig. 9 and 10 referring specifically to the drawn product.

The mechanical properties of dispersion strengthened materials are critically dependent upon both the nature and extent of the mechanical working processes applied to them during manufacture. This effect has been described with particular reference to platinum in a previous article in this journal (1). Processes such as swaging and drawing are particularly effective in inducing a highly aligned recrystallisation texture, and the properties achieved from ZGS platinum wires fully reflect the benefits to be derived.

Resistance measurements have been made by the four-terminal method on ZGS platinum wires 0.2 mm in diameter at temper-

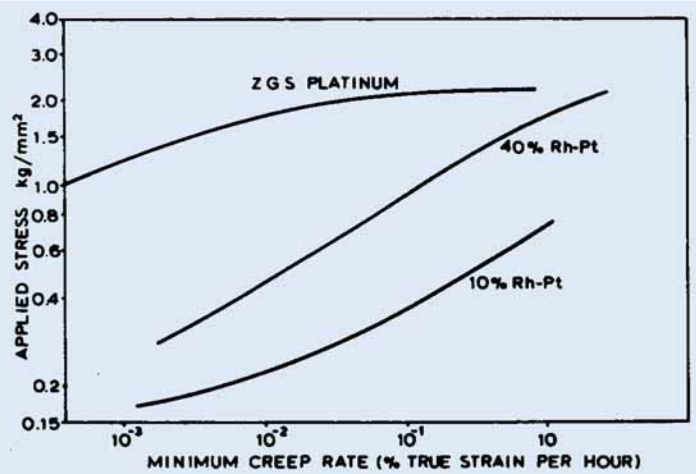


Fig. 10 Minimum creep rate data for ZGS platinum wire at 1400°C. Curves illustrating the performance of 10 and 40 per cent rhodium-platinum under similar conditions are included for comparison

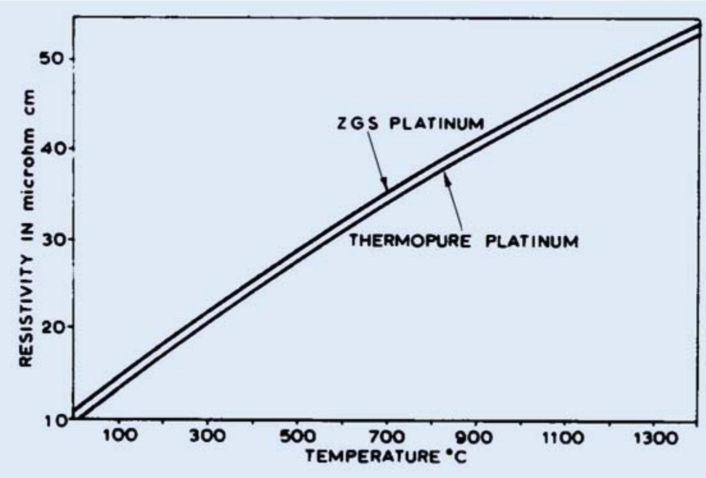


Fig. 11 Specific resistance of "Thermopure" and ZGS platinum wires as a function of temperature

atures up to 1400°C. The results are plotted in Fig. 11 which indicates that for all practical purposes its electrical characteristics resemble those of pure platinum.

Design Considerations – The Assembly of ZGS Apparatus

The importance of careful design studies in all cases where ZGS platinum is being considered as a material of construction for high temperature use cannot be overemphasised. Only in rare instances has it been possible to make a direct replacement of an existing alloy in an existing application without some modification to either design or construction procedure.

The joining of dispersion strengthened metals, either to themselves or to other materials, has been one of the problem areas which have prevented the full exploitation of their obvious potential. Conventional fusion welding processes destroy the fine oxide dispersion, upon which the high temperature properties depend, in the vicinity of the weld. The tendency has been, therefore, to consider the use of processes which effectively produce joints without melting – diffusion bonding, pressure deformation bonding and so on. While such techniques have given only limited success in the case of dispersion strengthened base metals, due to the presence of interfering oxide skins, they can be applied very easily and effectively to a metal such as platinum, which is completely free from surface oxidation products even at high temperatures. Figure 12 shows a simple lap joint produced by hot impact bonding two sheets of 0.5 mm thick ZGS platinum. The total reduction in thickness occasioned by the bonding process in the joint area was less than 15 per cent but a perfect join, across which recrystallisation occurred without hindrance during subsequent annealing, was formed.

In many applications it has been possible, from a consideration of the total design of a component, to avoid the use of non-standard joining procedures, either by eliminating welds altogether – the excellent formability of ZGS has been a tremendous advantage in this connection – or by resiting them in low

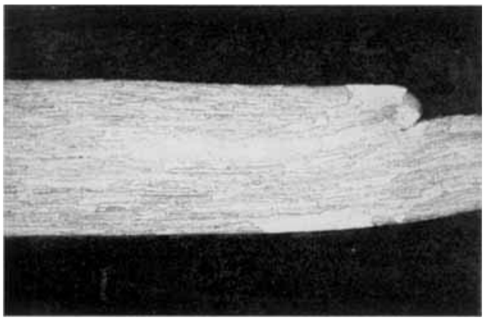


Fig. 12 Simple lap joint produced by hot impact bonding two sheets of ZGS platinum 0.5 mm thick. × *20*

Fig. 13 Four platinum crucibles fabricated by Johnson Matthey Metals Limited. The left-hand pair was made from conventional platinum 0.25 mm thick. The used crucible was in laboratory use for three months – large grain structure and deformation caused by handling are evident. The right-hand pair was made from ZGS platinum 0.15 mm thick and weighs 40 per cent less than conventional crucibles. The used crucible was also in general laboratory use for three months but the grain structure is fine and it has retained its original shape

temperature, lightly stressed regions where the operating demands are less severe. In the case of mixed material designs, it is only necessary to ensure that the joint is at least as strong and durable as the weakest component, and here again simple variants of conventional welding processes can be used to advantage.

The primary decision which must be made, of course, before detailed considerations such as joint design are entered into, concerns the technical and economic viability of using ZGS platinum, in preference to the more conventional materials for high temperature devices.

Applications

The developments described above clearly provide the equipment designer with a radically improved material of construction and in the long-term it is to be hoped that ZGS platinum will form the basis for a new generation of equipment operating effectively in air for long periods at temperatures in excess of 1000°C.

Glass fibre manufacture is a particularly good example of a technology which relies very heavily on the use of high temperature platinum alloys for glass handling purposes. The economics of glass fibre production are greatly dependent upon the efficiency of the fibre forming process, and generally favour the use of a bushing which delivers thousands rather than hundreds of filaments. The baseplates of such bushings need to be longer and wider than the majority of those currently in use, and a limiting factor preventing a general move to larger units has undoubtedly been the relatively poor resistance to creep induced distortion of the conventional alloys. ZGS platinum can clearly play a useful role in such an application. It has been introduced into existing bushings designs with some success, as illustrated in Fig. 1. An indication of its potential is provided by the fact that in several instances it has been possible to employ it in a fully self-supporting role as a baseplate material, thus eliminating the need for cumbersome support members in a critical area.

On strength considerations alone one might expect dramatic improvements in performance when ZGS platinum is used as a direct substitute for pure platinum, and this has indeed been the case when relatively highly stressed items such as optical glass stirrers have been constructed in the new material. In some instances, however, the life of a com-

Fig. 14 A glass holding bowl approximately 50 cm diameter and 30 cm deep. Formerly made from 10 per cent rhodium-platinum sheet 0.030 inch thick, it is now made from ZGS platinum 0.025 inch thick. The use of ZGS platinum is expected to double the life of the bowl

ponent is determined by factors other than strength or creep resistance. Contamination is one of the life-determining factors that have prompted the use of ZGS platinum in a predominantly weight-saving role, and an interesting example of this approach is provided by Fig. 13, which shows four platinum laboratory crucibles, two in pure platinum and two, 25 per cent lower in weight, in ZGS platinum. The distortion which characterises the used melted platinum crucible after a prolonged period of use is almost completely absent in the lightweight ZGS platinum version.

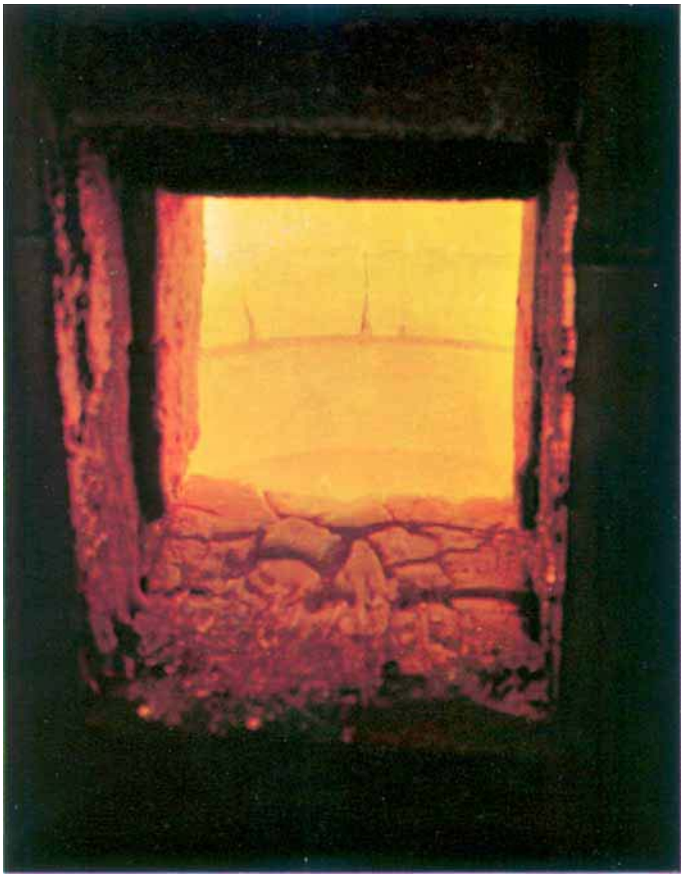
An item in which an excellent compromise was achieved between the hitherto conflicting requirements of a minimum capital holding and an economic service life is illustrated in Figs. 14 and 15. This glass holding bowl was formerly constructed in 10 per cent rhodium-platinum alloy from sheet 0.030 inch thick. The ZGS platinum unit shown in Fig. 14 has 0.025 inch thick walls, and preliminary operating experience in the glass holding furnace shown in Fig. 15 suggests that a twofold increase in service life is likely to be achieved. The main body of the bowl was constructed from four sheets of ZGS platinum. Joint strength was achieved by bonding these together using a hot impact welding technique.

The new material is giving interesting results in many other areas of platinum usage. While ZGS platinum cannot be regarded as a universal solution to all the problems encountered in industrial platinum practice, it can provide considerable benefits of real and lasting value.

Acknowledgments

This work was initiated by Dr A. S. Darling and much of it was undertaken by a team under his leadership. We are grateful for help in experimental work and mechanical testing by J. J. Alldridge and K. Majumdar.

Fig. 15 A glass holding furnace in operation. Within it can be seen the ZGS platinum glass holding bowl filled with molten glass. Long-term contact between high quality molten glass and rhodium-platinum alloys can lead to contamination of the glass by rhodium pick-up, while the use of pure platinum has obvious disadvantages on account of its low creep strength at high temperatures. The use of ZGS platinum in the handling of molten glass is thus an ideal application of the new material



References

1 A. S. Darling, G. L. Selman and A. A. Bourne, *Platinum Metals Rev.*, 1968, **12**, (1), 7–13
2 *British Patent Appl.* 3425/70
3 *British Patent* 1,280,815; *U.S. Patent* 3,696,502
4 *British Patent* 1,134,492
5 A. A. Bourne and A. S. Darling, *Platinum Metals Rev.*, 1963, 7, (2), 42–48

Topics at the Catalysis Society Meeting

The 3rd North American Meeting of the Catalysis Society, held in February at San Francisco, included 55 papers, many of them dealing with the platinum group metals.

Continued high interest in these metals for automobile emission control was evident from the symposium on catalytic problems relating to the environment, including papers from oil companies: Union Oil Co. of California—D. P. McArthur on "Activity, Selectivity and Degradation of Auto Exhaust NO_x Catalysts", and Mobil Corp.—D. Liederman et al. on "Deactivation Study of a Platinum Monolithic CO/Hydrocarbon Oxidation Catalyst"; from automobile manufacturers: General Motors—R. L. Klimisch et al. on "The Chemistry of Degradation in Automotive Emission Control Catalysts" and on "The Dual State Behaviour of Supported Noble Metal Catalysts", and Ford Motor Co.—R. A. Dalla Betta on "Hydrogen and Carbon Monoxide Adsorption on Ruthenium"; and from catalyst support manufacturers: Corning Glass Works—C. H. Bartholomew on "Reduction of NO by Monolithic-supported Pd-Ni and Pd-Ru Alloys". J. Turkevich et al. of Princeton University described "ESR Investigation of Adsorption of Oxygen on Silica, Palladium and Gold Surfaces". A related general paper by R. J. H. Voorhoeve et al. of Bell Laboratories dealt with "Perovskite-like $LaMnO_3$ Substituted with Potassium or Ruthenium for Reduction of Nitric Oxide."

General papers covered ammonia oxidation over supported platinum, determination of catalyst surface areas, deuterium exchange over noble metal powders, platinum-catalysed ethylene hydrogenation and oxidations of platinum surfaces, and of ketals of sugar alcohols.