Composite Platinum Group Metals

A NEW STRUCTURAL MATERIAL FOR GLASS HANDLING EQUIPMENT AND LABORATORY APPARATUS

By M. S. Rowe

Johnson Matthey Inc., Malvern. Pennsylvania

and A. E. Heywood

Johnson Matthey Metals Limited, Wembley, Middlesex

The cost of platinum and platinum-rich alloys inevitably leads to attempts to find cheaper alternative materials, particularly for applications where they are used for structural purposes. Previous work has generally centred on coating base metals with platinum or on the development of palladium-rich alloys. However, both of these approaches have limitations particularly with regard to strength, corrosion resistance and reliability. The application of zirconia grain stabilised technology to this problem has now resulted in the production of a composite trimetallic material, designated ZGS Platinum "TriM". This largely overcomes the problems associated with earlier materials and dramatically reduces material costs.

The industrial use of platinum and rhodium-platinum alloys is well documented. Their strength, formability and unique corrosion and high temperature oxidation resistance characteristics make them ideally suited to applications such as glass fibre bushings, claddings for glass handling equipment, bursting discs and laboratory apparatus. In most of these applications the alloys are used as structural members in their own right.

A major factor in the use of platinum or platinum-rich alloys is the significant cost of the metal. When this is allied with its high density the investment involved in even such simple pieces of apparatus as laboratory crucibles is considerable, although much of the cost may be recovered later. As a result many attempts have been made to replace rhodium-platinum with composites produced by plating or bonding techniques, or with cheaper alloys. Generally, replacing platinum with platinum-coated base metals has proved unsuccessful due to high temperature diffusion of the base metals into the platinum where their subsequent oxidation results in embrittlement and eventual failure of the platinum cladding.

Among the alloys considered palladium-platinum-rhodium alloys in particular appeared to show promise as cheaper alternatives to the rhodium-platinum alloys. However, when they were critically examined for current industrial use it was found that they did not provide any appreciable advantage for major applications. A comprehensive review of the properties of palladium and potentially useful palladium based alloys has been reported in this journal previously (1). Invariably it was found that the greater volume of material required to compensate for the reduced mechanical properties meant that no economic benefit resulted. With the large scale commercial exploitation of grain stabilised alloys in the 1970s another approach became available, namely to use high strength materials such as ZGS platinum (2) and ZGS rhodium-platinum (3) but with a related reduction in the thickness employed. This approach relied essentially on the utilisation of the greatly improved high temperature tensile creep strength of grain stabilised alloys. However, the reduction in wall thickness meant that the stiffness of the article was somewhat reduced, particularly at ambient temperature when the mechanical properties of grain stabilised materials approximate to those of the basic alloy. Where the inherent high strength of ZGS alloys was to be used to the full no reduction in thickness was made and therefore maximum advantage was gained.

The approach of using grain stabilised materials of reduced thickness has found wide acceptance for certain specific applications, such as for larger glass melting crucibles, where good support is provided by ceramic refractories. For some other purposes, however, practical limitations did not permit the full potential of grain stabilised alloys to be realised. These applications include those where handling of unsupported apparatus takes place, as in laboratory ware, or where direct electrical heating dictates a minimum cross-sectional area, for example fibre glass bushings, and for bursting discs where an unacceptably thin cross-section would result. Thus the requirement still existed to develop a high temperature material possessing the strength, stiffness, corrosion resistance and wetting characteristics of conventional platinum and rhodium-platinum alloys, allied with the lower metal cost of palladium-rich alloys.

Initially techniques such as fabricating honeycomb structures entirely from ZGS platinum and ZGS rhodium-platinum were considered. Although in theory the ease with which platinum alloys can be diffusion bonded made this a potentially attractive solution, the high cost of manufacture made it unacceptable in practice.

It appeared that a more practical solution would be to use relatively thin walled ZGS material and effectively increase its cross-section with a cheaper interlayer which would restore both stiffness and electrical conductivity. Base metals were examined as potential inner layer materials but, as with plated materials, diffusion into the platinum and subsequent oxidation remained a problem. In addition attempts to form composites with the more likely materials, such as nickel and its alloys, were unsuccessful due to inherent differences in both working and electrical characteristics. The cheaper noble metals such as ruthenium, palladium and rhodium (the latter being less costly than platinum on a volume basis) were also tested, and the properties of palladium were found to be the most suitable. A family of composite trimetallic materials made from ZGS platinum and palladium was developed and named ZGS Platinum "TriM" (4).

ZGS Platinum "TriM"

This new product is a composite material consisting of two zirconia grain stabilised platinum outer layers bonded to a palladium core. The outer layers of "TriM" provide high temperature strength and resistance to both grain growth and corrosion while the cheaper palladium core, which makes up the bulk of the composite, gives good rigidity and electrical conductivity.

Depending on the application, the thickness, and hence the weight, of the ZGS platinum layers is selected: 30, 40 or 50 per cent of the total composite weight being typical. For the 40 per cent composition the weight of the ZGS platinum is 40 per cent of the total with 20 per cent bonded to each side of the palladium core, which weighs 60 per cent of the total weight. The total weight is however significantly less than for the equivalent volume in platinum due to the lower density of palladium, see Table I.

For light duty applications, where the primary requirements are to prevent oxidation and provide corrosion resistance rather than high strength, thin layers of ZGS platinum are sufficient.

Thicker layers of ZGS platinum can be used where higher stresses or greater amounts of corrosion and erosion are anticipated. Whatever the requirement specific composite proportions can be produced to satisfy the need.

Palladium was selected as the core material for several very important practical reasons:

Table I

Relative Densities of ZGS Platinum "TriM" Composites Compared to Pure Platinum

Material*	Material density g/cm^3	Composite density relative to platinum density per cent	Platinum content of composite relative to the same volume of pure platinum weight per cent
Platinum	21.45	—	—
ZGS Platinum "TriM" 15:70:15	13.85	64.6	19.4
ZGS Platinum "TriM" 20:60:20	14.58	68.0	27.2
ZGS Platinum "TriM" 25:50:25	15.41	71.8	35.9

* The ratios given for ZGS Platinum "TriM" represent the relative weights of ZGS platinum: pure palladium: ZGS platinum in the composite

1. As a noble metal its intrinsic oxidation resistance is superior to that of base metals, even though it lacks the absolute oxidation resistance of platinum.
2. Metallurgically palladium is compatible with platinum, and as a result diffusion bonding is a reliable means of producing the composite.
3. The melting point of palladium (1552°C) is sufficiently close to that of platinum (1769°C) to make it suitable for a significant number of the demanding applications where platinum is generally used.
4. Palladium and platinum are equally ductile, so that complex forming operations are technically possible.
5. Historically, palladium is significantly cheaper than platinum being, typically, only about one-third of the price.

The Production of ZGS Platinum "TriM"

In view of the compatibility of platinum and palladium, a number of joining techniques were possible including brazing, explosive bonding, diffusion bonding and hot roll bonding. Of these, a combination of the last two was found to be the most cost effective. The basic composite is produced by sealing a palladium ingot into a ZGS platinum envelope to give a total thickness of approximately 10mm, the individual thickness of the two materials being in the proportions required in the final composite. Diffusion bonding is then carried out at a temperature of 900°C, and is followed by hot rolling to a thickness of 1.5mm. Further reduction to the required size is done by cold rolling.

Metallurgical Considerations

Prior to field trials it had been foreseen that the performance of ZGS Platinum "TriM" might be limited by excessive diffusion of palladium into the ZGS platinum layers, its significance depending on the thickness of these layers, as well as on the temperature and the period of operation. In practice, however, while some Kirkendall diffusion effects were encountered at temperatures higher than 1100 to 1200°C, these did not prove to be deleterious with correctly designed components.

Some Physical Properties of ZGS Platinum "TriM"

The densities of standard ZGS Platinum "TriM" composites are given in Table I together with the corresponding proportions of ZGS platinum and palladium, expressed as a percentage of composite weights. The designation 15:70:15 indicates a three layered composite consisting of, in weight per cent, 15 ZGS platinum, 70 palladium core and 15 ZGS platinum. The three composites all have a significantly lower density than pure platinum.

Stress-rupture tests were carried out on several ZGS Platinum "TriM" composites at a stress level of 1400 psi, and at temperatures

Table II

Stress-Rupture Results from ZGS Platinum "TriM" Composites and Pure Platinum

Applied Stress: 1400 psi

Material	Time to fracture, hours			
Pure platinum	5.1	1.19	0.23	0.035
ZGS Platinum "TriM" 15:70:15	50.8	8.40	2.40	0.280
ZGS Platinum "TriM" 20:60:20	224.3	20.0	4.80	0.80
ZGS Platinum "TriM" 25:50:25	637.7	107.0	20.60	3.40
Test temperature, °C	1000	1100	1200	1300

between 1000 and 1300°C. The times to fracture are given in Table II. These initial results show that even the composite with the lowest weight ratio of ZGS platinum provides an almost ten-fold increase in rupture life compared with pure platinum, at the test temperature. This is a most satisfactory improvement to result from replacing a significant amount of platinum with cheaper palladium and strengthening the composite with ZGS platinum. In Figure 1 the stress rupture properties of 25:50:25 ZGS Platinum "TriM" are compared with those of pure platinum, pure palladium and 10 per cent rhodium-platinum.

Stress-rupture tests of diffusion bonded ZGS platinum and palladium provided further information on their compatibility, which is the criterion that ultimately determines how well ZGS Platinum "TriM" can be formed and fabricated, and how it will perform in service. Evidence of the suitability of this type of bond manifested itself in all the test pieces examined, no cracking or separation of the outer ZGS platinum layers from the palladium cores being detected.

Field Trials

Laboratory Apparatus

Analytical laboratory apparatus was selected to introduce ZGS Platinum "TriM" composites to potential users, because the properties of these new materials seemed to be ideal for this application where intermittent operation at temperatures up to 1300°C is typical and good corrosion and erosion resistance are required. Experience has now shown that ZGS Platinum "TriM" can replace pure platinum in most analytical applications. Trials are continuing, and some apparatus has already provided

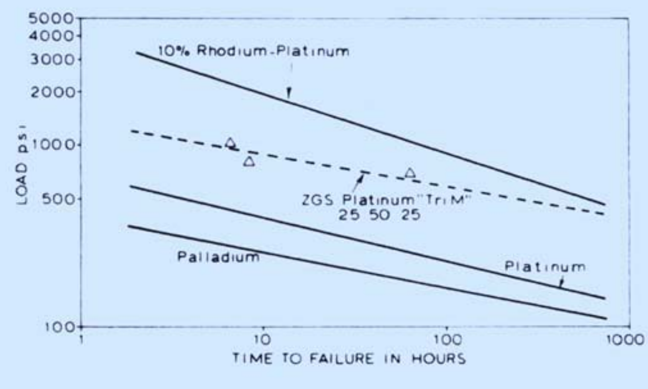

Fig. 1 A comparison of the stress rupture properties of the new composite material with pure platinum and palladium, and also with 10 per cent rhodium-platinum

satisfactory service over two years. Determinations involving sodium carbonate, sodium metaborates, hydrofluoric and sulphuric acids at temperatures up to 1100°C have been made daily without any detrimental effects being observed. A laboratory crucible produced in ZGS Platinum "TriM" by Johnson Matthey Metals Limited is shown in Figure 2.

In addition, ZGS Platinum "TriM" trays have been used to support ferrite components during furnace treatment, where previously pure platinum had been used. These trials also proved to be very successful.

The Glass Industry

In addition to laboratory apparatus, it was thought that ZGS Platinum "TriM" could be usefully employed in the glass manufacturing industry for certain selected applications. Trials of glass furnace start-up bushings have been carried out. These bushings need only serve for approximately three or four weeks while the poor quality glass that is melted during the start up period is drained from the furnace. The bushing is full of glass at all times, at a temperature of approximately 1250°C. Upon removal, the trial bushings showed no signs of corrosion, erosion or cracking. Clearly ZGS Platinum "TriM" is ideal for this purpose.

This success has led to the trial of another type of bushing which is used to feed a rotary type glass fibre process where once again the bushing is full of glass at 1250°C. Such bushings need to serve for a minimum period of six months, and a life in excess of one year will ultimately be required. At present ZGS Platinum "TriM" feeder bushings have served for seven months, and trials are continuing.

Bursting Disc Foils

A relatively small but none the less vital use of platinum is as thin foils used in bursting discs (5). These devices must burst only at a predetermined level, when the safe working pressure in a process vessel is exceeded. The excellent resistance to corrosion of platinum makes it ideally suitable for arduous applications where corrosive conditions may be

Fig. 2 This laboratory crucible, with a capacity of 30ml, is made from the new Johnson Matthey Metals' composite material ZGS Platinum "TriM". The core of palladium is sandwiched between two layers of zirconia grain stabilised platinum. The latter provides the necessary high temperature strength and resistance to both grain growth and corrosion while the cheaper palladium core gives the good rigidity required for this application

encountered at elevated temperatures. However, the relatively high strength of platinum dictates that for many purposes the foil used must have a very thin cross-section. During manufacture annealing may cause grain growth to occur to such an extent that a single grain traverses the total thickness of the foil; when this occurs the bursting properties of the foil may vary to an unacceptable degree, so rejection rates during production can be high. Previous attempts to replace platinum with materials having reduced grain growth characteristics, such as ZGS platinum, were not entirely satisfactory for a number of reasons. Now, however, trials with ZGS Platinum "TriM" have shown that consistent bursting results, with extremely small standard deviations, can be obtained and at lower metal costs.

Additional "TriM" Materials

Although ZGS Platinum "TriM" is still being introduced to potential users other "TriM" materials are already under consideration by Johnson Matthey. These would provide different properties and include composites with surface layers of ZGS 10 per cent rhodium-platinum for even greater strength, and ZGS 5 per cent gold-platinum outer layers to decrease wetting by molten glass (6).

Conclusion

ZGS Platinum "TriM" composites are new materials offering many industrial users of platinum considerable benefits including lower metal costs. Present and future developments of noble metal composite materials will widen their industrial application with worthwhile advantage to the customer.

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A Review of Catalytic Combustion

One of the most important applications of platinum group metals catalysts is for catalytic combustion, an improved, flameless, combustion process. Since traditional flame combustion or oxidation occurs only within specific air:fuel ratios and often produces pollutants it can be hard to control and may be incomplete. The use of a heterogeneous catalyst allows greater control of oxidation over a wide range of air: fuel ratios, and less pollutants are produced. In operation, the mixture of fuel and air is passed over the catalyst at a temperature which is sufficiently high to allow total oxidation to occur. With the correct catalyst technology this temperature is significantly lower than that required when the catalyst is not present. The reaction that occurs on the catalyst surface liberates both energy and the products of combustion. For hydrocarbon fuels the latter are carbon dioxide and water, which may be discharged to the atmosphere.

Catalytic combustion is used in a number of applications. The prime reasons for the combustion may be either to liberate energy in catalytic heaters, catalytic boilers and catalytic gas turbine engines, or it may be to remove or limit the formation of pollution by the use of car exhaust catalysts or industrial catalytic clean-up units. A most useful and readable review of the whole field of catalytic combustion, by Professor D. L. Trimm of the University of New South Wales, has recently been published in *Applied Catalysis,* 1983, 7, (3), 249–282.

This review concentrates on some of the less well known applications of catalytic combustion in low and high throughput units. For many of the applications one, or more, of the platinum group metals forms the preferred catalyst.

Gas turbines require a hot gas stream as their power source and this can be provided by catalytic combustion. The review covers in detail the published work in this field, giving information on the catalyst systems that have been used. The major advantages of catalytic combustion demonstrated are the reduction in the amount of nitrogen oxides formed when combustion occurs at temperatures less than 1650°C and the ability of catalytic combustion to take place with leaner air:fuel ratios than are required for flame combustion.

The various washcoat systems that are used to provide the high surface area upon which the catalytic metal can be deposited are considered; these include the favoured monolithic, or honeycomb, supports. The review, which also covers the kinetics of catalytic combustion, a consideration of low and high throughput systems, heterogeneous-homogeneous combustion and the use of alternative fuels, includes 133 references. R.A.S.