

# Advanced Coating Technology A.C.T.<sup>TM</sup>

## MORE EFFECTIVE USE OF THE PLATINUM METALS WILL BENEFIT THE GLASS MANUFACTURING INDUSTRY

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The glass industry manufactures a multitude of products ranging from domestic glass tableware to "high tech" optical glass. In its most basic form, such glass is a combination of soda lime and silica with additions of modifiers and refiners, and when molten it is a very aggressive substance. During product manufacture much of the process equipment is subjected to severe environments, which may involve high temperatures, or corrosive chemicals, or both, and equipment will be in contact with both liquid glass and the glass vapour. In view of this, difficulties are encountered in the containment, handling and processing of glass. A need therefore exists for materials which have excellent corrosion resistance and good stability at high temperatures; such properties are typical of the platinum group metals.

At first sight, transition metals, such as nickel and iron, and the refractory metals molybdenum and tungsten, with their excellent mechanical properties and modest cost, make ideal candidates for use in the glass industry. The refractory metals, notably molybdenum, are very useful in the molten glass environment, but only under strictly controlled conditions. The poor resistance to oxidation of transition metals and their alloys, however, results in apparatus having only a limited service life, leading to premature failure and colouring of the glass, see Figure 1.

By comparison, the refractory oxides (ceramics) have high temperature stability but they suffer from relatively poor mechanical properties, notably brittleness and poor thermal shock resistance, and moderate resistance to corrosion by molten glass. The intrinsic disadvantages of lim-

ited thermal shock resistance, combined with spallation and dissolution in the glass melt, restrict their use.

The best combination of properties for use in the molten glass environment are provided by the platinum group metals and their alloys, which are characterised by high melting points and excellent chemical nobility. Platinum is one of the most inert of the group, and it is relatively non-reactive with most glass melts up to approximately 1450°C; however, the service life of conventional platinum alloys may be limited at higher temperatures by grain growth. Over many years, a range of zirconia grain stabilised (ZGS) alloys, which contain very fine, uniform dispersions of oxide particulates, has been developed by Johnson Matthey (1). Such dispersions restrict microstructural degradation and effectively extend the operating life at these higher temperatures. The manufacturing process for ZGS alloys promotes the formation of a high aspect ratio grain structure. This elongated structure is extremely stable even at very high temperatures and results in alloys which exhibit the highest tensile strengths, creep properties and general durability levels of all comparable platinum group metals and alloys, see Figure 2; thus they are eminently suitable for use in the glass industry (2).

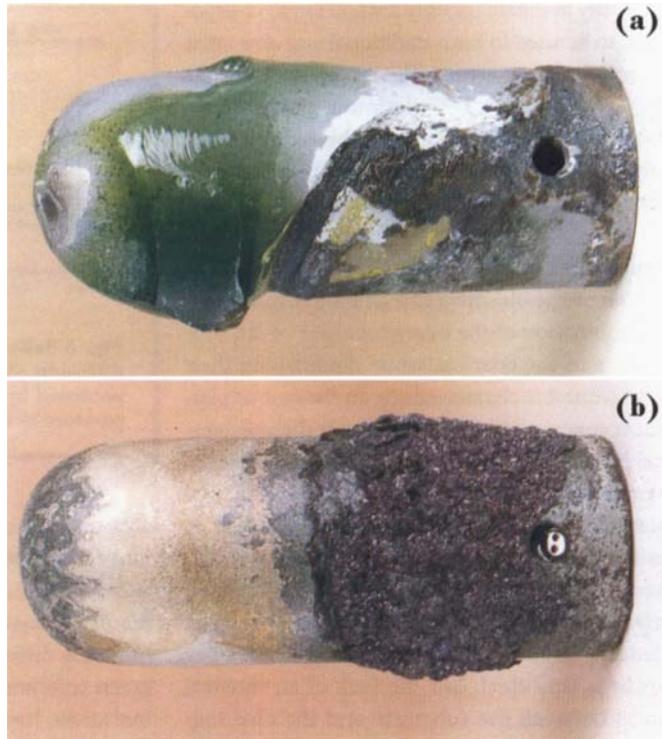
The use of ZGS platinum group metals and alloys has enabled cost effective solutions to be achieved for a wide range of industrial problems. There are, however, a number of other applications for which the platinum group metals would provide the ideal technical solution, but where, because of their intrinsic value, the advantage gained would be insufficient to justify their use in bulk.

In some instances, alloying platinum group metals with base metals can be used to obtain

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**Fig. 1** Two examples of nickel-chromium alloys shown after partial immersion glass testing at 1200°C for 100 hours. The use of unprotected nickel can result in the early failure of equipment and discoloration of the glass being processed

(a) shows corrosive attack at the air/substrate/glass interface and (b) shows build-up of oxide resulting from gross oxidation of the nickel alloy in the glass vapour

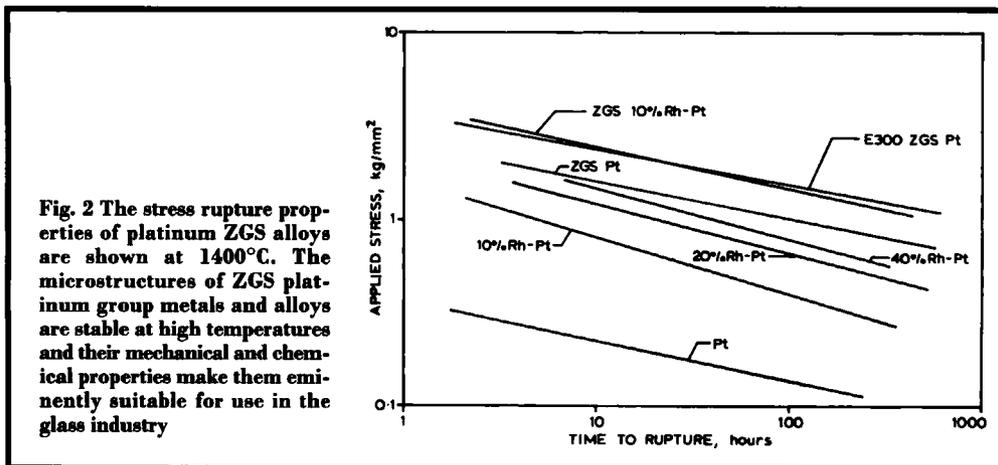


improved mechanical properties and decreased costs, but there is a related reduction in resistance to the harsh conditions encountered in service.

For components of relatively simple shape one solution has proved to be the use of platinum group metal claddings on ceramic or base metal

substrates in place of bulk platinum group metals. This has resulted in reduced cost components with appropriate properties.

Now, new Advanced Coating Technology (A.C.T.<sup>TM</sup>) (3), which is being introduced by Johnson Matthey, will allow the advantageous properties of platinum group metal claddings,



**Fig. 2** The stress rupture properties of platinum ZGS alloys are shown at 1400°C. The microstructures of ZGS platinum group metals and alloys are stable at high temperatures and their mechanical and chemical properties make them eminently suitable for use in the glass industry

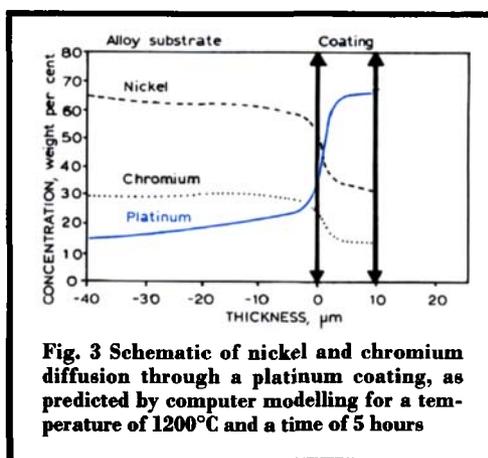
currently available for only a small range of products, to be used in both traditional and new areas of application, especially on more complex shapes. This A.C.T.<sup>TM</sup> platinum group metals coating technology will extend the existing fused salt and aqueous Q-salt plating (4) capability of Johnson Matthey.

### Coating Technology

The prime objective of a coating is to achieve a combination of the best properties of the substrate and the coating, while diminishing their less favourable characteristics. In the case of platinum coatings, the aim is to retain the mechanical properties of the substrate and confer on it the beneficial environmental resistance provided by platinum. By coating with platinum, the poor corrosion resistance of the substrate is improved, while the high density and the cost are lowered relative to those of bulk platinum. Mechanically cladding a substrate with platinum goes part way towards this ideal, but the lack of an integral bond between the substrate and the cladding means that the two materials act independently. However, the intimate nature of A.C.T.<sup>TM</sup> coatings enables them to develop synergistic characteristics with the substrate.

At high temperatures the use of coatings or claddings is potentially limited by their interaction with the substrate. This interaction is predominantly controlled by diffusion and can lead to rapid degradation of the coating, with significant loss of properties (5). The whole A.C.T.<sup>TM</sup> process has been modelled by computer using available diffusion data (6) and standard equations. This enables predictions to be made of the likely behaviour of various combinations of materials, over chosen temperature ranges and times, although these can only serve as a general guide to the actual performance of the materials under service conditions.

One example of a computer modelled prediction of how nickel and chromium could be expected to diffuse through a platinum coating is shown in Figure 3. The prediction indicates that after only 24 hours at 1200°C there would be extensive diffusion of both base elements into a 10 µm platinum layer. Actual nickel-chromium



**Fig. 3 Schematic of nickel and chromium diffusion through a platinum coating, as predicted by computer modelling for a temperature of 1200°C and a time of 5 hours**

substrates, plated with 15 and 25 µm of platinum, are shown in Figure 4 after partial immersion for 24 hours in molten glass at 1200°C. The platinum coatings have been degraded by the outward diffusion of nickel (indicated by the green coloration) and also by the effects of thermal stress, leading to total disruption in the case of the thinner coating. Thus experimental behaviour was comparable with the predictions of the model, which was subsequently used to develop more complex coating systems able to overcome the problem of diffusion. Following extensive laboratory experiments and trials of systems selected on the basis of predictions from the models, a complex coating system designed to overcome the effects both of diffusion and differential thermal expansion between substrate and coating has been developed.

The make-up of the coating system is dependant upon the substrate to be protected and the intended service environment. For example, to protect nickel-chromium type substrates the coating consists of several distinct layers, each of which has one or more functions:

(i) To offset any mismatch between substrate and protective outer layer, which results from variations in thermal expansion characteristics. The strains arising from such differences can be large and must be accommodated by the ductilities of the interlayers together with their thermal expansivities.

(ii) To slow interdiffusion between the

**Fig. 4** The effects of 24 hours partial immersion in molten glass, at 1200°C, on a nickel alloy coated directly with platinum; (a) shows glass line disruption of a 15 µm platinum coating and (b) shows diffusion of nickel and chromium through a 25 µm coating of platinum



constituents of the outer protective coating and the underlying substrate material. Such inter-diffusion is usually deleterious.

(iii) To key the other layers together in order to improve mechanical integrity.

The total coating thickness may be as low as 250 µm, but it can be substantially greater. Of this thickness, 150 to 200 µm is usually platinum

or a platinum group metal, although this could be varied significantly depending on the specific service requirements.

#### Testing the Coatings

The A.C.T.<sup>TM</sup> coating system was designed to enhance the surface properties of substrates with inherently good mechanical properties and/or

**Fig. 5** The working end of a platinum A.C.T.<sup>TM</sup> coated tri-level thermocouple assembly after 2800 hours of forehearth service at 1200°C



thermal stabilities at high temperatures. Considerable laboratory testing of such coatings was undertaken before the work was extended to include field trials of protected nickel-chromium alloys. This work was performed in forehearths of major glass container companies in the U.K. and in Australia. With typical molten glass temperatures of between 1100 and 1200°C, substrate protection was achieved for up to the maximum test time of 4500 hours, Figure 5.

It was recognised that this technology was limited by the strength of the substrate material at high temperatures, which in the case of nickel-chromium alloys imposed an upper temperature limit of 1200 to 1250°C. This temperature maximum would limit the applications of the coated materials to only a fraction of their potential uses in the glass industry. Attention was therefore transferred to the development of protection for higher temperature substrates, namely the refractory ceramics.

#### A.C.T.<sup>TM</sup> Coatings on Ceramics

The technology developed to provide protective coatings for nickel based alloys was extended further to allow its application to some of the many varieties of refractory ceramic substrates (7). Mullite tubes, closed at one end, were used as substrates in the first trials, which were performed at temperatures up to 1350°C. During this phase of laboratory testing the thickness of

the platinum in the protective coating system was between 150 and 400 µm. Failure of the alumina crucibles used to contain the molten glass limited the duration of tests to about 500 hours at 1200°C, and to 100 hours at 1350°C.

Components coated using the A.C.T.<sup>TM</sup> system were subjected to extensive investigation and analysis in tested and untested conditions. Only after this were field tests undertaken using A.C.T.<sup>TM</sup> on tri-level thermocouple assemblies, see Figure 6. The early field tests were undertaken in a forehearth operated by a glass container manufacturer, and the first components were subjected to temperatures of up to 1200°C in molten flint, amber and green glasses, in succession. Sufficient confidence was gained in the performance of these coated tri-level thermocouples to allow their use as part of an integrated system for glass temperature control. Now in its eleventh month of use, the A.C.T.<sup>TM</sup> coated assembly is still "problem free".

An example of a mullite substrate protected by a 10 per cent rhodium-platinum A.C.T.<sup>TM</sup> system is shown in Figure 7.

Following the first field tests, further components have been tested in forehearths at various glass plants located around the world. These trials have involved mullite substrates, and various thicknesses and compositions of platinum group metal A.C.T.<sup>TM</sup> coatings have been used to provide the protection over different lengths of the

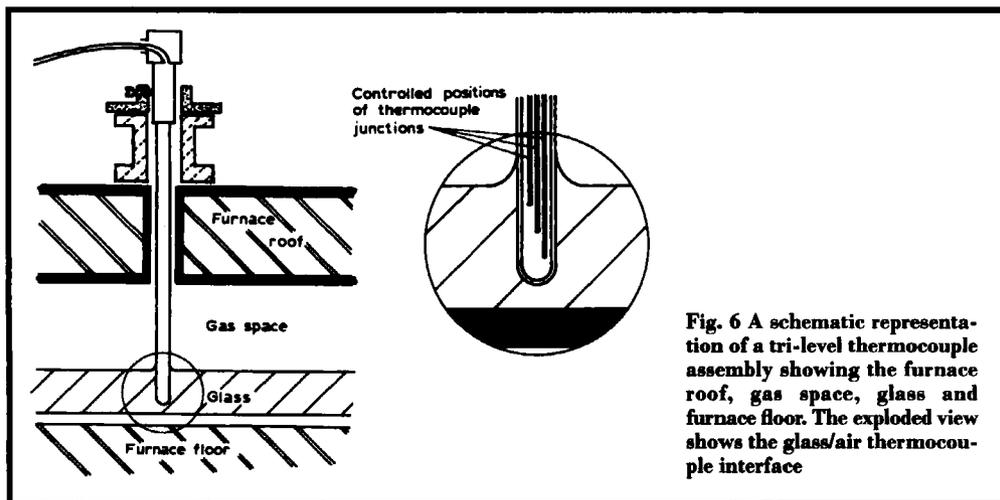
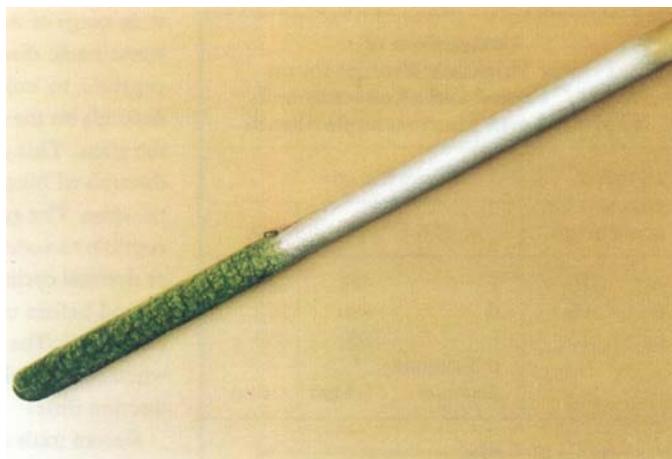


Fig. 6 A schematic representation of a tri-level thermocouple assembly showing the furnace roof, gas space, glass and furnace floor. The exploded view shows the glass/air thermocouple interface

**Fig. 7** The working end of a tri-level thermocouple assembly with part of the mullite tube A.C.T.<sup>™</sup> coated with 10 per cent rhodium-platinum, shown after 1000 hours of forehearth service



component. All have performed extremely well, and have even shown some unexpected additional benefits. For example, one user has observed significant reductions in the “noise” associated with thermocouple readings, compared with that from conventional products having the same protected length.

Although much of the research and development work used mullite as a substrate, other refractories have also been successfully protected by A.C.T.<sup>™</sup> systems. These have ranged from high purity alumina to almost pure silica, including materials such as zircon-mullite and alumina-silicates. Work to extend the variety of substrates which can be protected by A.C.T.<sup>™</sup> systems is now being undertaken.

Within the glass industry this technology could be applied to the protection of a wide variety of components including the rotors for fibre glass production, bubbler tubes, electrodes, skimmer blocks, flow control devices, gobbing units, stirrers, orifice rings and other special delivery-forming equipment and furnace furniture. Commercialisation has now begun, primarily for thermocouple sheathing.

### **The Tri-Level Thermocouple Assembly Design**

The protection of thermocouples is the starting point for the commercial application of A.C.T.<sup>™</sup> technology. This is particularly directed at the arduous service environments associated

with the intrusive monitoring of glass temperatures either in forehearth or in melting furnaces (8, 9). One important sub-group of thermocouples is the tri-level thermocouple.

In this particular application the benefits resulting from the use of A.C.T.<sup>™</sup> on thermocouple assemblies in preference to conventional cladding include the ability to customise a standardised basic assembly design with:

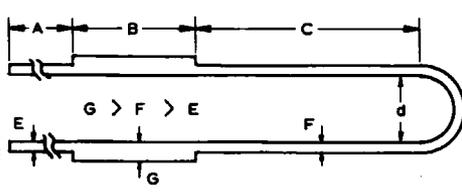
- variable assembly length
- variable coating length
- variable coating thickness profiles
- variable composition of the coating material.

Thus the specific requirements of a customer can be rapidly fulfilled.

### **The Financial Benefits of Using A.C.T.<sup>™</sup>**

In addition to the technical benefits resulting from the integration of the substrate and the protective metal coating, the A.C.T.<sup>™</sup> system also confers the potential for significant financial benefits to accrue from the more effective use of the platinum group metals. First, protective A.C.T.<sup>™</sup> coatings can be prepared at thicknesses down to 175  $\mu\text{m}$ , which compares favourably with the lower limits for conventional cladding procedures, which are about 350 to 400  $\mu\text{m}$ . Secondly, platinum group metal layers of 400  $\mu\text{m}$  thick, or more, can easily be achieved by A.C.T.<sup>™</sup> over critical areas of components where enhanced durability or other specific properties are required for a particular application. Importantly, A.C.T.<sup>™</sup>

Comparison of Typical Thickness Profiles for an A.C.T. <sup>TM</sup> Coated and a Conventionally Clad Tri-Level Thermocouple Sheath				
Length of segment for coating, cm		Thickness, $\mu\text{m}$		
		A.C.T. <sup>TM</sup>		Clad
A	15	E	175	350
B	5	G	350	350
C	10	F	200	350
		d Substrate diameter	1.4 cm	1.4 cm



technology enables the thickness of the platinum group metal coating, and thus the protection provided, to be matched to the various service conditions encountered at different parts of the same component.

Typical dimensions of A.C.T.<sup>TM</sup> and conventional coatings used on a traditional design of tri-level thermocouple sheath are shown in the Table, while the cost benefits, see Figure 8, which may result from the more effective use of the platinum group metals can be deduced from the Table by a comparison of the relative weights of the metals used.

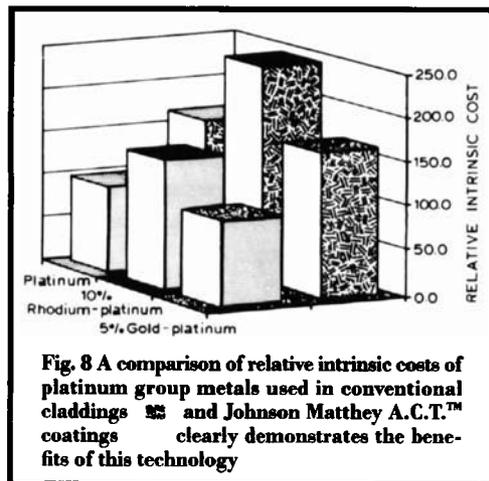
### Gathering Balls

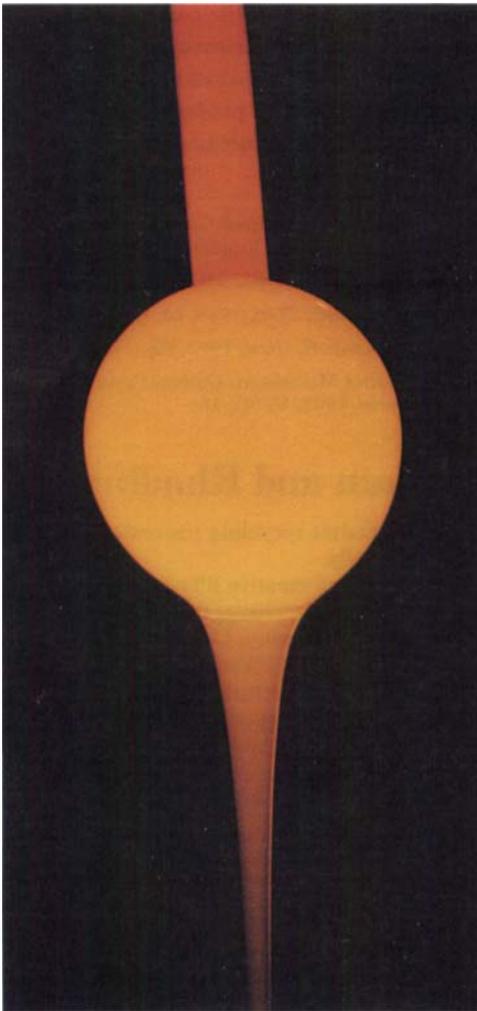
The transfer of molten glass into moulds can be accomplished by a number of techniques, with the selection being based on the volume and speed of the required transfers. At low rates a gathering or transfer ball is used (10); this utilises the rotation of the ball and the viscosity of the melt to achieve "carry over" of the glass. Traditionally iron balls were used – a natural extension of the blowing iron, but more recently ceramic balls were introduced, mainly to eliminate problems resulting from contamination of the glass with iron. These balls are available in a

wide range of sizes and compositions but all have some basic disadvantages, such as being susceptible to corrosion, the severity of which depends on the composition of both the ball and the glass. This corrosion may result in the production of blisters and perhaps even stones in the glass. The gathering balls also tend to be susceptible to sudden failure due to thermal shock or thermal cycling, so they must be carefully pre-heated before use and maintained hot between campaigns. The operating regimes required, even when successful, cause considerable loss of production time.

Recent trials of gathering balls made of selected ceramic substrates clad with A.C.T.<sup>TM</sup> platinum coatings, see Figure 9, have shown that considerable progress has been made in overcoming the problems discussed above. In addition to overcoming corrosion, gathering balls with coatings of 200  $\mu\text{m}$  nominal thickness have demonstrated excellent glass transfer characteristics, have enabled start-up times to be minimised and have shown tolerance to repeated stop-start cycles.

To date trials have been performed in borosilicate glasses and in lead crystal, with operating temperatures in the range 1200 to 1400°C. To enable the gathering balls to be examined, trials have now been curtailed after several weeks of operation. An evaluation of the potential for using A.C.T.<sup>TM</sup> on transfer balls is still being carried





**Fig. 9** A platinum A.C.T.<sup>TM</sup> coated ceramic gathering ball streaming molten glass, during service trials

out, and the potential benefits of using platinum group metal alloys as alternatives to platinum are also being examined and assessed.

#### **Other Components**

One of the exciting aspects of the A.C.T.<sup>TM</sup> coating technology is its versatility. It can be applied to a wide range of component shapes. Indeed the major benefits of the technology to users are expected to occur from the elimination or reduction of component failure, which otherwise results in major production downtime. Many of these components are complex in shape and

therefore not amenable to cladding by the traditional techniques. On such shapes A.C.T.<sup>TM</sup> will allow the utilisation of platinum group metals, and their use will be readily justified by the ensuing extension of component operating life and/or improvement in product quality.

A large component coated with 10 per cent rhodium-platinum alloy by A.C.T.<sup>TM</sup> has been supplied to a major European glass manufacturer.

#### **Summary and Conclusions**

Despite their inherent disadvantages, notably brittleness, poor thermal shock resistance and poor resistance to molten glass corrosion, the refractory ceramics have for many years been the preferred materials of choice for equipment used in the glass industry. In many of their applications satisfactory performance is achieved by regular replacement. In other situations, platinum and its alloys, which are also accepted as essential materials for the fabrication of crucial components, are used to clad the refractory ceramics with a protective coating. The use of cladding is, however, limited by the complexity of the shape of the substrate which can be satisfactorily clad, and by the minimum thickness which can realistically be applied.

These restrictions can be overcome by A.C.T.<sup>TM</sup>, so there will be opportunities for A.C.T.<sup>TM</sup> platinum group metal coatings on ceramics to progress into areas of glass production technology where the cost of bulk platinum group metals has inhibited their use, or where the process of cladding is too unwieldy, or indeed technically non-feasible.

Platinum group metal A.C.T.<sup>TM</sup> coatings have several advantages over cladding:

- Easier and more effective protection of difficult-to-clad intricate shapes
- Thinner platinum group metal layers, leading to lower metal costs
- Thickness profiling of platinum group metals
- Elimination of cementing or mechanical fixing of protective layer to substrate
- Elimination of welding platinum group metals
- Use of alloys which are not amenable to cladding.

As in any industry, the glass manufacturers

are not only looking to improve the quality of their product but also to achieve economies in production.

To these ends, the benefits which users of A.C.T.<sup>TM</sup> coatings should derive will include

improved reliability of the coated component, improved thermal shock resistance, reduced down times, and generally maintained or improved quality of the glass end product, with respect to both defects and to dimensional tolerances.

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## Availability of Platinum, Palladium and Rhodium

In view of their widespread use in the automotive, chemical, electronic and petroleum industries the platinum metals are regarded as strategic materials in the United States of America. For this reason the U.S. Bureau of Mines collects and evaluates information relating to their availability and demand. A previous report from this organisation was published in 1982, based on data — from the so-called market economy countries — available up to 1980 (1). Since then major changes have occurred in the supply of these metals as the industry prepared to satisfy the increased demand expected to result from new anti-pollution legislation, particularly in countries of the European Community.

This earlier study has now been updated following a complete re-evaluation of resources, industry structure and costs (2). Based on 1989 data, the new report commences with an overview of supply and industrial demand for platinum, palladium and rhodium. A further section considers the resources, cost and economic factors that affect the availability of the platinum metals, and includes pricing and price proportion analysis, and availability analyses. Data are presented in a total of thirty-four figures and tables, and this main part of the report is supported by 106 references.

In an appendix, demand and uses for the platinum metals are summarised. Environmental uses are regarded as some of the most critical of the many industrial applications; demand for jewellery and investment are also considered. In other appendices the methodology employed in this study is explained, the major mining properties in Southern Africa and North America are described, and mining, treatment

and autocatalyst recycling processes are summarised briefly.

This most informative fifty-four page report is available without charge from: Chief, Branch of Minerals Availability; U.S. Bureau of Mines; 810 7th Street, NW; Washington, DC 20241-5202; U.S.A. For technical information, contact Catharine T. Fogg or Joseph L. Cornellison at the Minerals Availability Field Office; U.S. Bureau of Mines; Building 53, Denver Federal Center; Denver, CO 80225; U.S.A.

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## Ultra Micro Glutamate Sensor

Microbiosensors based on semiconductor fabrication technology are of the order of millimetres in size, but significantly smaller electrodes are required for insertion into the brain or nerve tissue. Now researchers in Japan have constructed an integrated ultra micro enzyme sensor with a 7  $\mu\text{m}$  diameter platinised carbon fibre disc electrode and a platinum thin film counter electrode (E. Tamiya, Y. Sugiura, T. Takeuchi, M. Suzuki, I. Karube and A. Akiyama, *Sens. Actuators B*, 1993, 10, (3), 179–184).

The surface of the carbon fibre electrode was platinised electrochemically, which increased the electrode activity sufficient for the sensor to be used for the determination of glutamate, an important neurotransmitter.