Dispersion Strengthened Gold-Platinum

A NEW MATERIAL FOR GLASS HANDLING EQUIPMENT

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Platinum alloys containing gold exhibit marked non-wetting characteristics with molten glasses. Simple gold-palladium alloys, however, are relatively weak while those that have rhodium added to increase their strength can be difficult to work, and also suffer from embrittlement during service. Now the binary alloys can be dispersion strengthened with zirconia to produce a material with the ductility of the simple binary and the higher hot strengths of rhodium-containing ternary alloys. This dispersion strengthened gold-platinum alloy has enhanced resistance to progressive contamination and offers a longer service life. It is being used successfully for specialised applications in the glass industry, for which it has potential, as well as for the apparatus in which samples for X-ray fluorescence analysis are prepared.

The marked effect that gold has upon the contact angle between a platinum surface and molten glass is well documented. In particular, Selman, Spender and Darling carried out considerable work on this subject using soda glass and 'E' glass—a glass commonly used for the production of reinforcement fibre (1,2,3). The remarkable increase in contact angle that the addition of gold produces, particularly at levels of 3 per cent and above, is shown in Figure 1. Also of importance is the elimination of the contact angle "trough" that occurs with both platinum and rhodium-platinum alloys between about 900 and 1250°C, see Figure 2.

This phenomenon is not restricted to conventional glasses but is also seen with other glassy compounds such as the borate fluxes commonly used in the preparation of samples for X-ray fluorescence analysis (XRF) (4). As a result, gold-platinum and gold-rhodium-platinum apparatus is widely used in analytical and glass research laboratories.

The most common binary composition used is 5 per cent gold-platinum. Higher gold contents produce little further increase in contact angle, as can be seen in Figure 3, but can bring considerable problems with inhomogeneity due to segregation resulting from the considerable difference in solidus and liquidus temperatures in the gold-platinum system, as shown in Figure 4. For many applications the simple binary alloy has insufficient hot strength to give an acceptable service life and a ternary alloy of platinum, gold and rhodium provides increased strength and is commonly used in XRF analysis applications (4,5,6). The exact choice of alloy is, however, something of a compromise. An alloy of 5 gold, 10 rhodium and 85 per cent platinum provides good wetting resistance and strength, see Figures 5 and 6, but compared to the binary alloy is difficult to form and has inferior chemical resistance (4). Additionally, the grain boundary gold-rich precipitation noted during Selman's work is often realised in practice, particularly during the preparation of sample beads for XRF, leading to embrittlement and subsequent cracking. Reducing the gold content to 3 per cent but maintaining the rhodium content significantly reduces the problems of corrosion and embrittlement while retaining a useful strength; a relevant *U.S. Patent* 3,672,880 identifies platinum alloys with gold and rhodium contents in the ranges 1 to 3 per cent and 12 to 25 per cent, respectively.

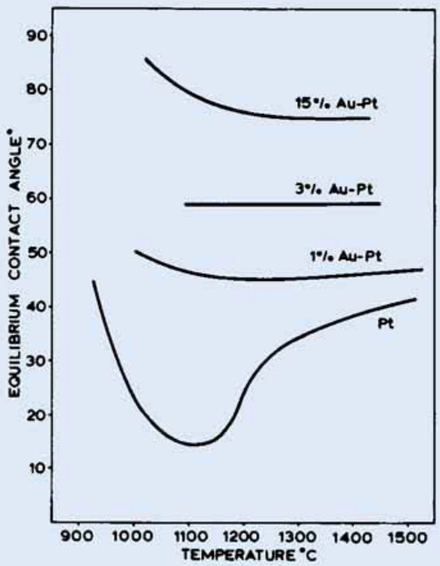

Fig. 1 The effect of temperature on the equilibrium contact angle of 'E' glass on three binary gold-platinum alloys and on platinum when heated in air (2)

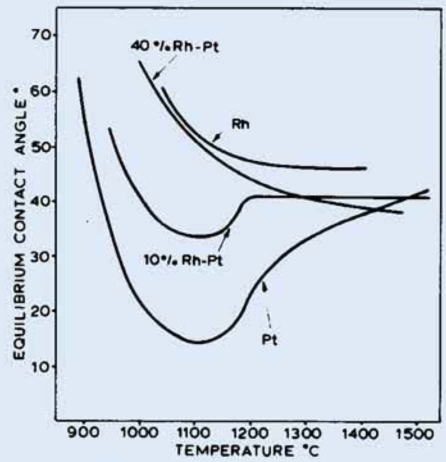

Fig. 2 The effect of temperature on the equilibrium contact angle of 'E' glass on rhodium-platinum alloys heated in air. Note the contact angle trough for the platinum, and for the 10 per cent rhodium-platinum alloy. Although high rhodium contents increase the contact angle at low temperatures, above 1200°C any increase is marginal (2)

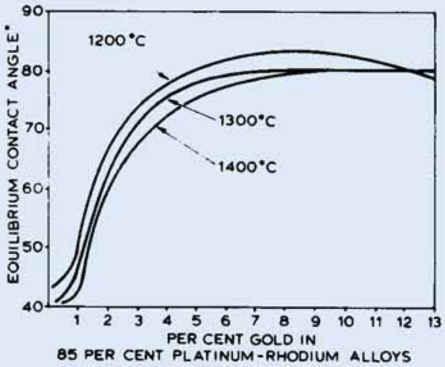

Fig. 3 The effect of gold on the equilibrium contact angle of 'E' glass on ternary alloys of platinum, rhodium and gold, containing 85 per cent platinum at the three given temperatures. Gold contents greater than 5 per cent do not produce any substantial increase in the contact angle (2)

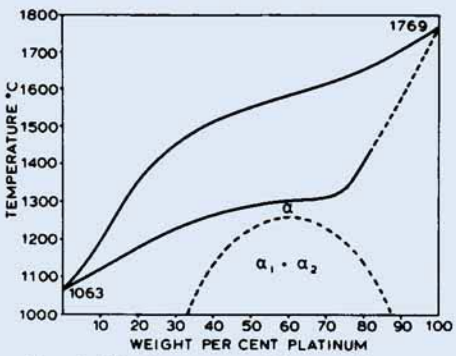

Fig. 4 The binary equilibrium diagram for alloys of gold and platinum showing the considerable differences between solidus and liquidus temperatures for alloys of intermediate compositions. After Max Hansen, "Constitution of Binary Alloys", published McGraw-Hill

However, the contact angle of such alloys is reduced as shown in Figure 3, and they are sensitive to any loss of gold from the surface.

All the alloys mentioned so far experience grain growth during use at typical service temperatures. This is particularly relevant to XRF analysis work in two respects, namely the surface finish of sample beads and also the ability to resist the effects of grain boundary contamination of the type described (7).

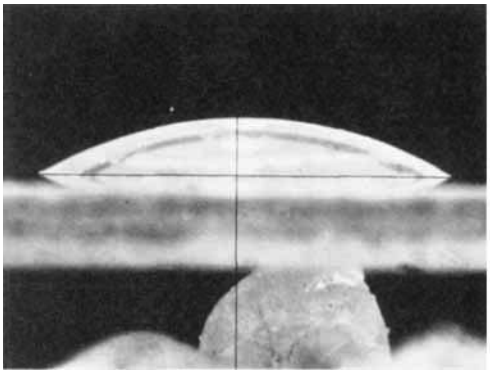

Fig. 5a A droplet of 'E' glass in equilibrium with the surface of a 10 per cent rhodium-platinum alloy heated in air at 1200°C showing a relatively low contact angle ×20

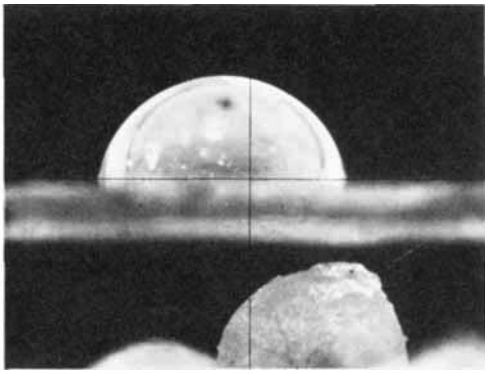

Fig. 5b The high contact angle assumed by a droplet of 'E' glass melted in air at 1200°C on the surface of 5 gold-10 rhodium-85 per cent platinum alloy (2) ×20

To attain a high contact angle, the binary alloy of 5 per cent gold-platinum represents the best option, and also has the benefit of being easily worked. Attempting to provide this alloy with good hot strength leads in turn to other problems outlined earlier, and no previously available option overcame the problem of grain growth. It was clear that a need existed for an alloy with the workability and wetting characteristics of 5 per cent gold-platinum but combined with the hot strength of the rhodium-containing ternary alloys; resistance to grain growth and progressive contamination resistance were also desirable. The solution lay in utilising the techniques developed by Johnson Matthey for the production of dispersion strengthened platinum and rhodium-platinum alloys (8,9). The dispersion of 0.08 to 0.1 per cent zirconia in the binary 5 per cent gold-platinum alloy, coupled with suitable thermomechanical treatment, resulted in the development of an alloy possessing the strength of the ternary alloys and the wettability and the ease of fabrication of the binary alloy. In addition, grain growth at service temperatures was dramatically reduced and the contamination resistance noted by Knapton was clearly demonstrated. This new material has been

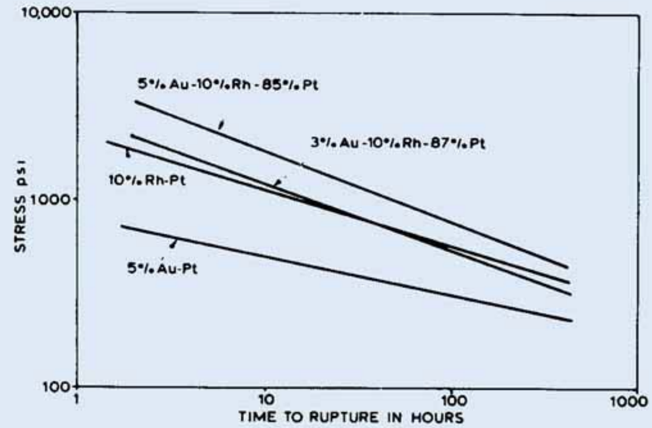

Fig. 6 Stress rupture data for various platinum alloys tested at 1400°C shows that the 5 gold-10 rhodium-85 platinum alloy has superior strength, particularly when compared with the simple 5 gold-platinum binary alloy

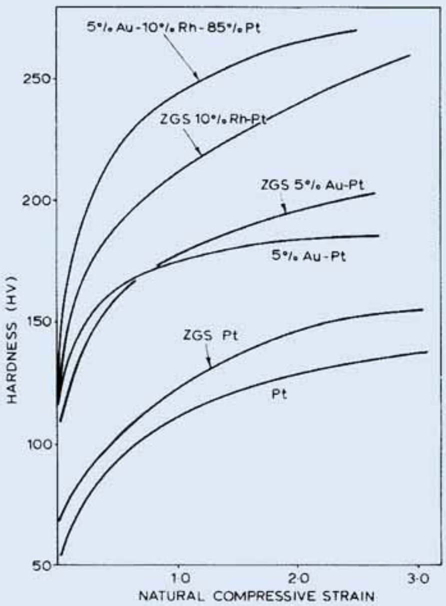

Fig. 7 (Above) The work hardening characteristics of ZGS 5 per cent gold-platinum compared with those of platinum and other platinum alloys

designated ZGS 5 per cent gold-platinum, and its ductility and stress rupture characteristics are given in Figures 7, 8 and 9.

The XRF Analysis Application

ZGS 5 per cent gold-platinum has been thoroughly evaluated in the market for which it was primarily developed, that is for making casting dishes used in the preparation of XRF sample beads. A typical moulding dish is illustrated in Figure 10. Service lives in the order of 4 or 5 times that of the conventional alloys have been reported (6). Additionally, and equally important, the surface finish of beads produced in casting discs made from this material is dramatically improved (see Figure 11) with a consequent improvement in analytical accuracy being reported in many

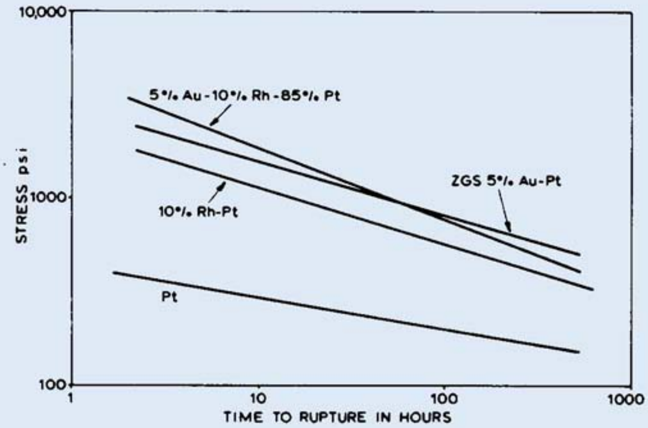

Fig. 8 Stress rupture data for ZGS 5 per cent gold-platinum compared with those of platinum and other platinum alloys, tested at 1400°C

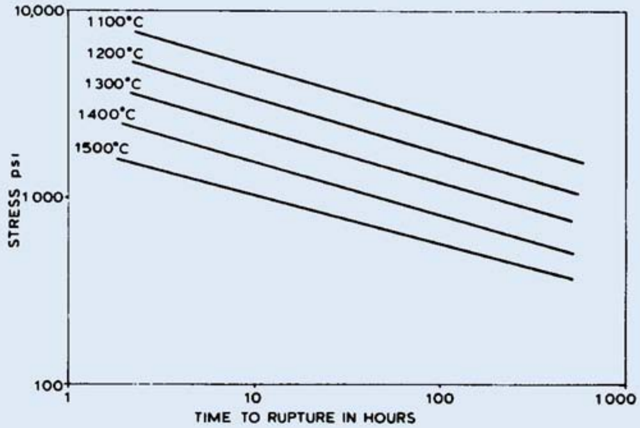

Fig. 9 Stress rupture data for ZGS 5 per cent gold-platinum at test temperatures between 1100 and 1500°C

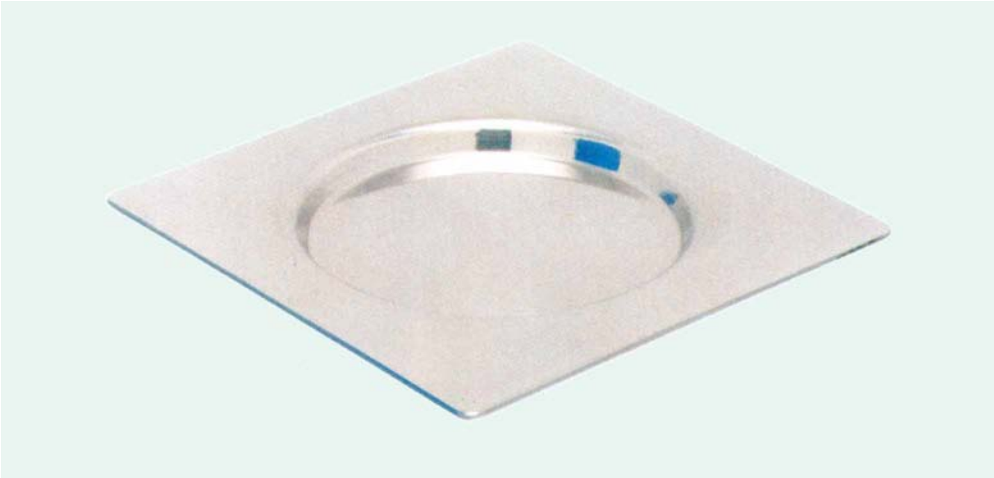

Fig. 10 A typical platinum alloy mould used for the preparation of XRF sample beads of the type shown in Fig. 11; high surface finish and flatness are important requirements

cases. As a result these dishes are particularly useful for the automated methods of analysis currently gaining wide acceptance for industrial purposes.

The superiority of ZGS 5 per cent gold-platinum over conventional alloys in this application is without doubt, and the response from the market confirms this, even though the alloy is more expensive to produce than conventional alloys. As a result the demand for ternary alloys has fallen considerably and it is not difficult to envisage a situation where gold-platinum is used for low temperature applications and ZGS gold-platinum at above about 800°C, rendering the troublesome ternary alloys redundant.

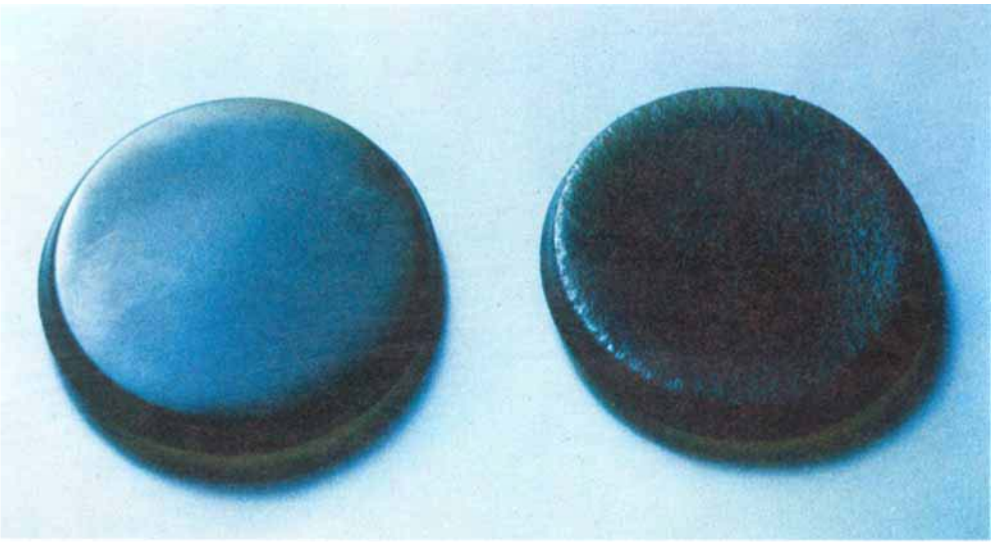

Fig. 11 XRF sample beads prepared in moulds that have been in service for some time. The bead on the left was prepared in a ZGS 5 per cent gold-platinum mould and shows a good surface finish. The poor surface finish of the bead on the right is the result of excessive grain growth in a standard gold-platinum mould during service; the illustrated surface is also noticeably concave

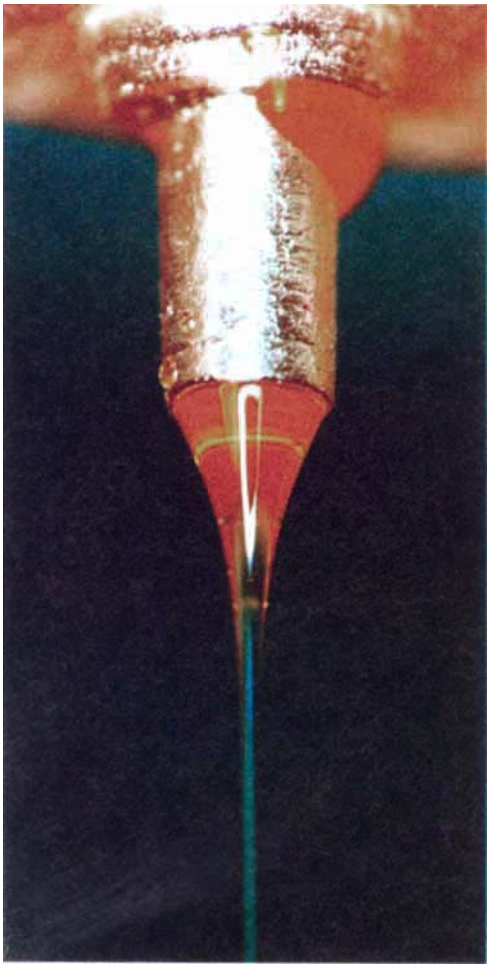

Fig. 12 Glass fibre filaments are formed by drawing molten glass through hundreds of small orifices in a bushing baseplate. The stability of the meniscus is critical in the successful operation of the process

Photograph by courtesy of Owens-Corning Fiberglas Corporation

Glass Fibre Production

The production of continuous glass fibre utilising platinum bushings as described by Loewenstein is a complex and highly skilled process (10). The stability of the meniscus illustrated in Figure 12 is greatly affected by the wettability of the alloy and the use of gold-containing alloys is an obvious development, either to improve the current designs or to enable jets to be more closely packed and hence increase bushing efficiency.

Of the previously available materials, the poor creep strength of the simple binary gold-platinum alloy precludes its use as a bushing baseplate material. Ternary alloys, especially 5 gold-10 rhodium-85 per cent platinum, would be difficult if not impossible to fabricate for this purpose by the existing coining and deep drawing method indicated in Figure 13. Although the wettability of 3 per cent gold-rhodium-platinum is better than that of both 10 per cent rhodium-platinum and 20 per cent rhodium-platinum the alloy has proved to be unstable in service due to the deleterious effect of any loss of gold, however small. This is clearly shown in Figure 3. Unfortunately, adding gold-platinum to a rhodium-platinum jet leads to the diffusion of gold into the baseplate during fabrication and use, so denuding the tip of the jet and reducing the contact angle.

The advent of ZGS gold-platinum has enabled "non wetting" baseplates having the strength of rhodium-platinum alloys to be produced by the existing method (11) and these have performed satisfactorily over a 12 month period. Initial trials were made with conventional designs where flooding of the jets was not necessarily a severe problem; nevertheless, the amount of glass contamination of the baseplate was dramatically reduced. Trials are

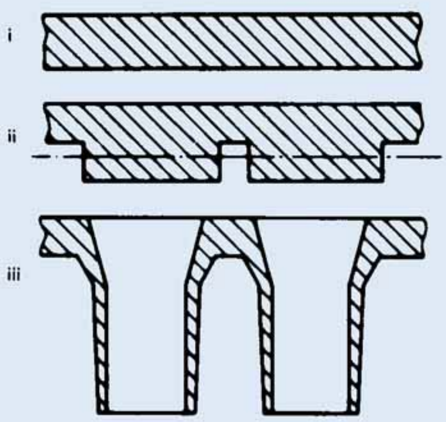

Fig. 13 A schematic diagram indicating how a bushing baseplate is made by coining (ii) followed by deep drawing (iii). After Loewenstein (10)

now proceeding with baseplates of more radical design which exploit the improved wetting characteristics of the alloys.

Conclusions

This extension of the ZGS process has resulted in the development of a new material, ZGS 5 per cent gold-platinum, that reconciles the hitherto conflicting needs of XRF analysis equipment, and which has considerably improved the performance of the apparatus and the product, and thus the accuracy of the results. The availability of this unique material has resulted in considerable interest from other markets, notably the glass fibre industry which foresees its use for the development of new high performance bushings for the production of continuous fibre.

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The Control of Nitrogen Oxides Emissions

PROGRESS REVIEWED AT INTERNATIONAL SYMPOSIUM

Nitrogen oxides (NO_x) emissions were first identified as major contributors to air pollution after studies made during the 1950s into the formation of photochemical smog in Los Angeles. These observations led directly to legislation in the United States of America regulating emission of NO_x to the atmosphere from both stationary and mobile sources. Since that time it has been recognised that such emissions constitute a global problem. A recent symposium sponsored by The Netherlands Ministry of Health and Environmental Protection and the U.S. Environmental Protection Agency, held in Maastricht during May, reviewed the state of the art in research and development relating to national and international policies on NO_x control. More than 300 delegates attended, demonstrating the current interest in the subject, and over 75 papers were presented.

The control of nitrogen oxides resulting from nitric acid production was the subject of papers presented by W. Toering of UKF, Rotterdam and A. Kayaert of Nederlandse Stikstof Maatschappij, based on their operational experience. Both pollution control and energy recovery result from the use of suitable platinum metal catalyst systems for the treatment of tail gases.

Emissions from mobile sources were considered in papers presented by H. D. Pletka of DEGUSSA, Hanau and A. E. R. Budd of Johnson Matthey Chemicals Limited. The latter traced the history of ceramic honeycomb supported platinum group metal catalysts from their first recorded industrial application in controlling NO_x emissions from the tail gases of nitric acid manufacturing plants, to the development of three-way catalysts for the simultaneous control of NO_x, carbon monoxide and hydrocarbon emissions in petrol engined vehicle exhaust gases. In addition, reference was made to the successful application of platinum group metals catalysts in catalytic combustion systems for both gas turbine and catalytic engines. Catalytic combustion, that is flameless combustion promoted by a catalyst, promises a number of advantages, including low NO_x emissions without the use of tail gas clean-up devices.

Catalytic clean-up devices are the best developed and most practical method of mobile NO_x emission control currently available, and it is probable that platinum group metal catalyst technology will continue to play an important role in the control of stationary sources of NO_x emissions for some time to come.

The full proceedings of the symposium, and the discussion, are to be published in October by Elsevier Scientific Publishing Company.