

# Noble Metal Catalysts on Metallic Substrates

## A NEW GENERATION OF CELLULAR MONOLITHS FOR EMISSION CONTROL

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*The use of platinum group metal catalysts supported on ceramic monoliths for control of gaseous emissions from automobiles and chemical plant is now well established. Research in the Johnson Matthey Laboratories and at AERE Harwell, aimed at meeting the demand for more effective catalysts, has resulted in a new generation of platinum catalysts in which the ceramic substrate is replaced by a metal monolith. These metal substrate platinum catalysts are found to be more compact and more efficient than conventional ceramic structures. At the same time they overcome the structural limitations of ceramics with greater resistance to thermal shock and mechanical failure. The development of the metal substrate catalyst, and its use in hostile high temperature environments such as automobile emission control and catalytic combustion is described.*

In recent years attention has been turned towards the effects of man and his technology on the environment, of which a major effect has been the reduction in air quality over the years. Corrective measures are being taken to reduce the emissions to the atmosphere from mobile and stationary sources such as automobiles, power stations and fossil fuel burners. Other controls are in force for chemical plant and major pollutant sources.

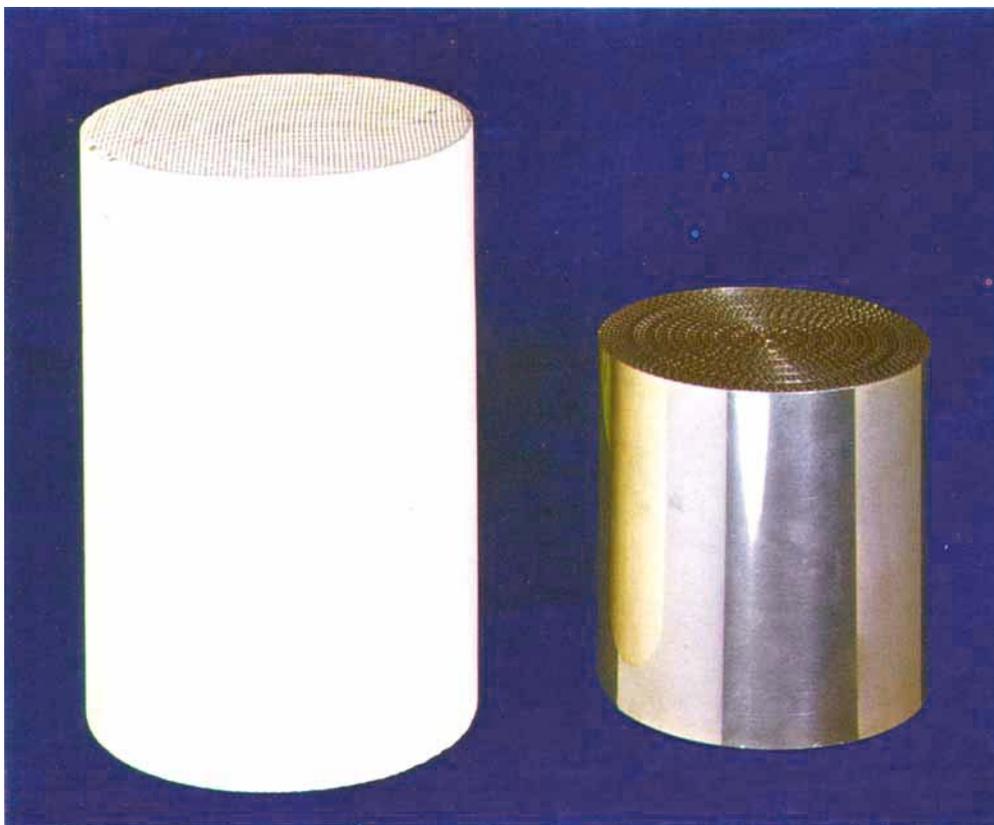
Effective emission control is often obtained by the use of noble metal catalysts (1-7), and to date the normal substrate for these catalysts has been a porous ceramic, either in pelleted or cellular monolith form. In general the ceramic monolith has gained greater acceptance in high-flow velocity operation due to the low pressure drop inherent in its configuration. However, the physical properties of these ceramic substrates are not ideal

since they are relatively fragile and liable to thermal shock fracture.

Platinum catalysts mounted on a metal substrate have been developed to overcome the mechanical and thermal limitations of the ceramic monolith. At the same time metal substrates possess the major advantage of higher surface to volume ratio giving increased reactivity per unit volume, while possessing lower pressure drop per unit length.

### The Metal Substrate Concept

In order to preserve the advantages inherent in the cellular monolith catalyst the metal substrate is designed to give axial flow passages throughout its length (Figure 1). This design yields maximum gas/solid contact for catalytic reaction, and maintains low pressure drop over the catalyst bed.



*Fig. 1 Comparable monolithic ceramic and metal catalyst substrates. The metal units have been developed to overcome the mechanical and thermal shock limitations encountered with ceramic monoliths. Additionally, a metal substrate only 3.5 inches diameter and 3.5 inches long gives similar catalytic performance to a ceramic substrate 4 inches diameter and 6 inches long*

Analysis of the parameters of such a structure in relation to catalytic performance reveals that two predominant processes govern the effectiveness of the catalyst. Under low temperature conditions, such as cold start on an automobile, the thermal mass of the catalyst must be kept low in order to assist rapid warm-up of the catalytic surface to its ignition temperature, whence emission control commences. Conversely under high temperature operation the rapid combustion of pollutant species occurs, and the rate limiting process becomes the mass transfer of reactants from the gas phase to the walls of the channel.

During mass transfer limited operation the overall conversion of the monolithic

catalyst is defined by the following equation:

$$\ln. f_R = f \left\{ K \frac{S/V \cdot C \cdot A \cdot L}{R} \right\}$$

where  $f_R$  is the residual emission

$S/V$  is the geometric surface area/unit volume of the monolith

$C$  is the function of the channel geometry  
 $A$  is the percentage open area of the inlet face

$L$  is the length of the monolith

$R$  is the hydraulic radius of the monolith channel, and

$K$  is a constant incorporating the reactant gas diffusivity, density and feed rate, and the cross sectional area of the reactor.

From the above equation it can be seen that as the monolith length, open area and

surface volume ratio is increased, and the channel hydraulic radius is decreased, the conversion over the catalyst will increase. Thus we may assess the performance gains of a metal substrate catalyst structure in terms of the advantages of manufacture from thin foil sheet (typically 0.002 inch) in comparison to ceramic structures containing thicker walls (typically 0.010 inch). Fabrication from thin metal sheet allows a much higher cell density (channels/in<sup>2</sup>) with a resultant increase in surface/volume ratio (S/V), hence increasing effectiveness per unit volume. Metal substrates are currently fabricated up to 600 cells/in<sup>2</sup> (see Table I) yielding a geometric surface area of 1190 ft<sup>2</sup>/ft<sup>3</sup> which is approximately double that of the ceramic monoliths currently in use. In addition the thin wall thickness allows significant increase in the open area of the monolith inlet face which again increases effectiveness and at the same time reduces the pressure drop per unit length. Channel geometry, and hydraulic radius may be optimised for maximal effect. Thus a metal substrate fabricated from thin sheet should compete effectively with its ceramic counterpart even when using significantly smaller catalyst volumes. Complete analysis of the interrelated parameters of mass transfer and

thermal mass reveals that a metal substrate 3.5 inch diameter × 3.5 inch long gives equivalent mass transfer characteristics to a 4 inch diameter × 6 inch long ceramic substrate and possesses lower thermal mass (Figure 1). The unit volume effectiveness of the metal substrate proves an attractive feature in automobile pollution control applications where space limitation is often an over-riding criterion (Figure 2).

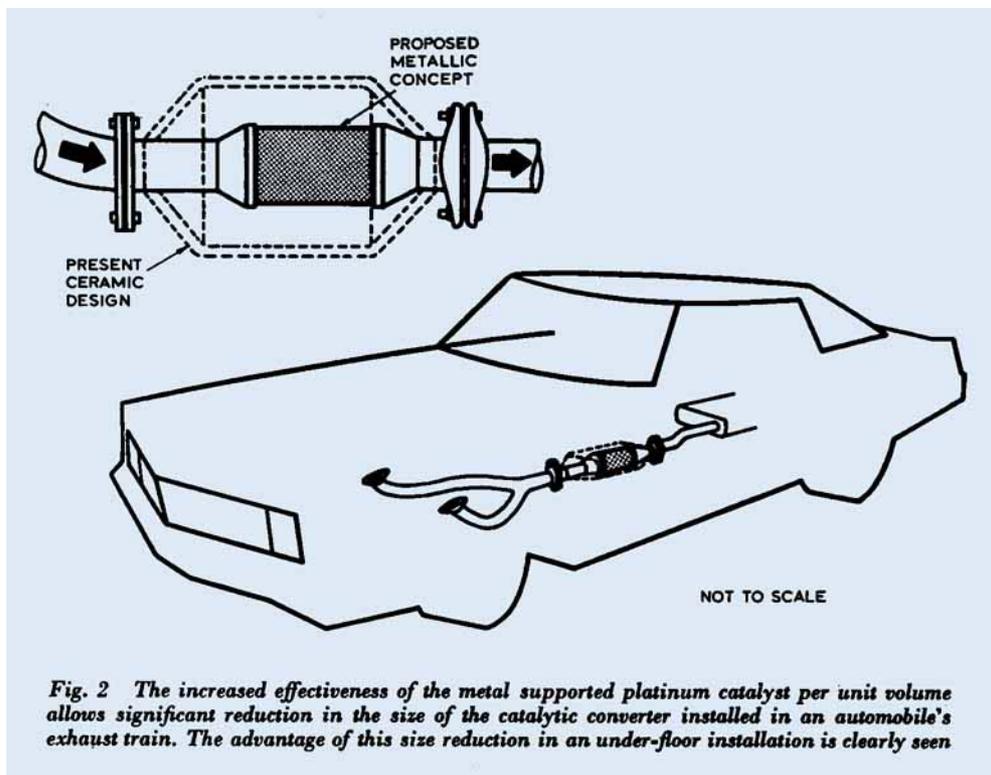
Improved durability of a catalyst mounted on a metallic substrate may accrue from its inherent resistance to mechanical and thermal failure, provided that the steel is resistant to oxidation and corrosion in high temperature exhaust environments, and the catalytic coating is compatible with the selected steel. The catalyst layer must also be resistant to abrasive attrition in high temperature, high flow, corrosive environments.

### Selection of the Steel

The operation of a metal substrate catalyst in high temperature oxidative and corrosive environments, typical of automobile exhaust conditions, requires that the alloy selected is resistant to corrosion and that any surface oxide film formed on the alloy is adherent and free from cracks. Oxidation

**Table I**  
**Comparison of Ceramic and Metal Substrate Parameters**

Parameter	Ceramic Cell Density cell/in <sup>2</sup>		Metal Cell Density cell/in <sup>2</sup>		
	200	300	400	500	600
Cell area, cm <sup>2</sup>	0.023	0.0143	0.015	0.011	0.0097
Surface to volume ratio per cm	18.9	22.05	32.3	35.8	39.4
Surface to volume ratio per ft	576	672	987	1090	1197
Open area, per cent	70	60	89	86	83
Wall thickness, cm	0.028	0.030	0.005	0.005	0.005
Wall thickness, inch	0.011	0.012	0.002	0.002	0.002



tests carried out on a series of alloys including (a) ferritic steels, (b) austenitic steels, and (c) non-ferrous alloys based on nickel-chromium, have revealed that the aluminium-containing ferritic steels are particularly attractive in this context.

Examination of the mode of surface oxide growth by scanning electron microscopy reveals the surface topography of some of the alloys considered for this application (Figure 3). The micrograph of an austenitic steel (top, left) shows the unsatisfactory nature of its surface for metal substrate catalyst applications. In this instance the surface oxide film has flaked from the surface and secondary oxidation of the underlying surface has commenced. X-ray analysis of a gold-palladium coated surface oxide film using an energy dispersive analyser (bottom, left) reveals that the surface film is predominantly iron oxide. Obviously attempts to catalyse this material to produce a durable catalyst

unit are likely to lead to loss of the noble metal catalyst as the underlying surface oxide layer spalls from the metal.

Examination of an aluminium-containing ferritic steel reveals a strong contrast to the austenitic steels. This steel shows significant surface oxide growth after high temperature treatment but X-ray analysis shows that the oxide growth is due predominantly to migration of aluminium (bottom, right) from the bulk alloy to the surface to form a protective adherent oxide layer with no evidence of surface cracks (top, right).

The excellent oxidation resistance of aluminium-containing ferritic steels demonstrated in the electron micrography studies was again confirmed by thermogravimetric analysis of thin foil sheet oxidised in air at temperatures up to 1200°C. Austenitic steel is shown to have an unacceptably high oxidation rate at 1200°C. Surface oxide fracture and reoxidation is evident from the point of

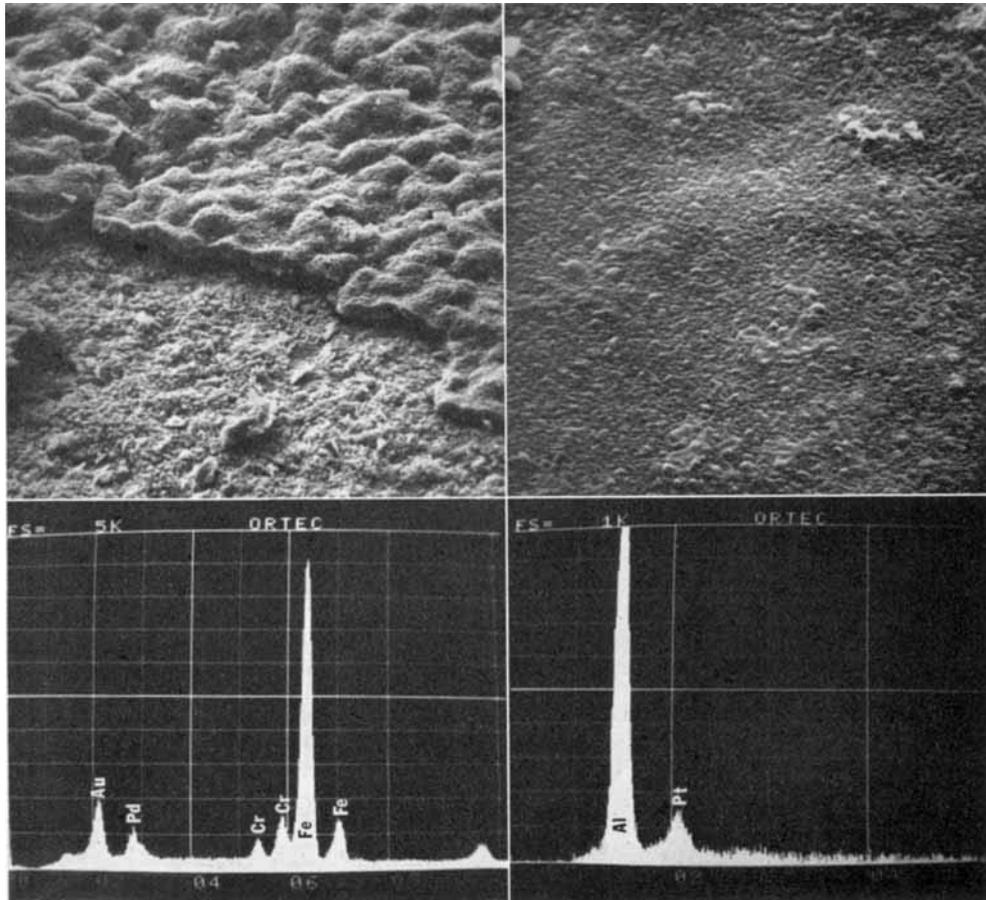


Fig. 3 Electron photomicrographs showing the surface topography of an austenitic and a ferritic steel after heat-treatment in an oxidising environment. The surface topography is shown on the two top photomicrographs where the austenitic steel (left) has been severely oxidised, and some of the oxide layer has spalled from the steel exposing a new surface to oxidation. On the other hand, the aluminium-containing ferritic steel (right) is covered by a continuous oxide layer which shows no signs of spalling or cracking. The energy dispersive analyser shows, in the lower photographs, the spectra obtained from the surfaces of the two materials. The oxide on the aluminium-containing ferritic steel (right) is mainly aluminium which has migrated to the surface to form a protective coating, while on the austenitic steel (left) the oxide is iron. The gold and palladium indicated are coatings applied for analysis purposes only

inflexion in the weight gain curve after 4 hours oxidation, Figure 4(a). In contrast the aluminium-containing ferritic steel, Figure 4(b), shows excellent oxidation resistance up to 1200°C.

As a result of these studies, coupled with an assessment of the viability of manufacture of the steel in thin foil form (thickness 0.002 inch), Fecralloy® steel was selected as the prime contender for a metal catalyst support

matrix. This alloy has been developed by AERE Harwell for automotive exhaust catalyst applications (8).

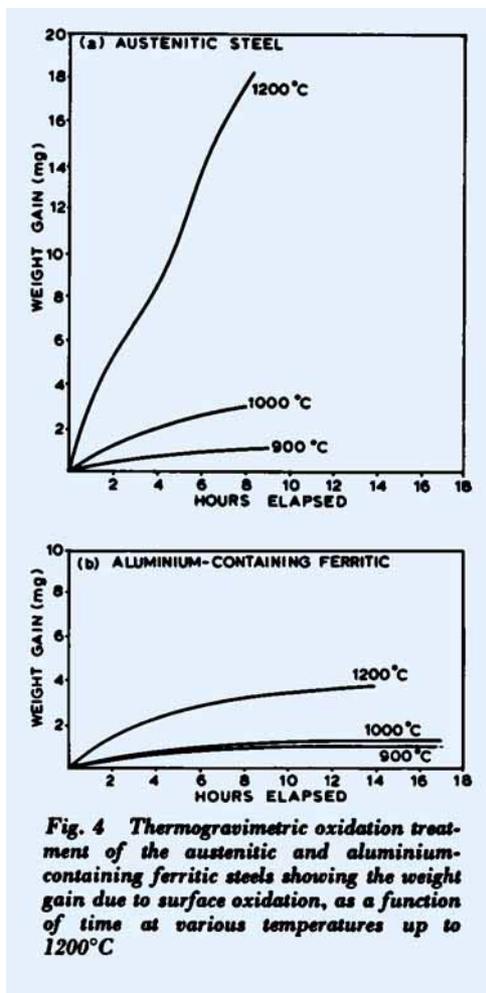
Fecralloy steels derive from a family of steels containing for example up to 20 per cent chromium, 0.5 to 12 per cent aluminium, 0.1 to 3 per cent yttrium and the balance iron, which on heating in air at typically 800 to 1000°C form an alumina-rich surface layer which endows the steel with excellent

high temperature oxidation resistance. For example, it can be used in various thicknesses at temperatures as high as 1200 to 1300°C in air with none of the surface spalling properties that tend to be associated with austenitic steels and some related commercial ferritic steels. Fecralloy steel sheet 0.5 mm thick has a life of over one year in air at 1200°C but, in common with other steels, maximum usable temperatures are lower in this environment. Nevertheless Fecralloy steel can be exposed to exhaust gases for periods of several hundred hours at temperatures as high as 1050°C. The excellent protective property of the alumina surface layer is thought to be enhanced by the influence of the yttrium.

Fecralloy steel, along with some other aluminium-containing ferritic steels, has the attraction of having an alumina coating which emanates from within the bulk of the material and is essentially self-healing, whereas alumina washcoats applied to conventional steels are prone to spalling on being subjected to repeated thermal cycling or mechanical vibration.

### Catalysing the Metal Substrate

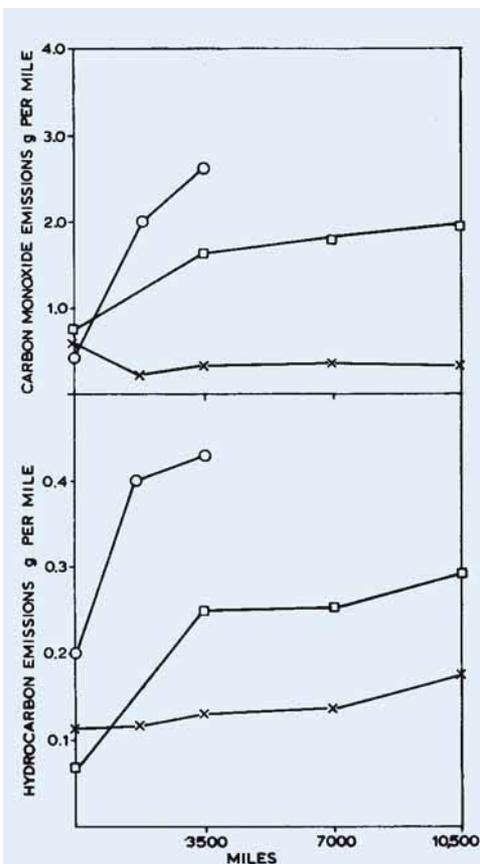
The conversion of the monolith metal substrate into an active noble metal catalyst entails deposition of the catalyst layer on the surface of the steel. Initial studies (Figure 5) rapidly revealed that simple deposition of platinum on to an oxidised steel surface was unsatisfactory in that although initial performance was comparable to the ceramic catalyst, the metal supported catalyst rapidly deteriorated during use. Further studies showed that the deactivation process could be prevented by deposition of platinum on to a high surface area gamma alumina (designated the catalytic alumina layer), bonded to the surface of the steel. Proprietary techniques have been developed to achieve the firm bonding necessary to overcome spalling of the catalytic alumina layer due to differential thermal expansion of the substrate steel and the alumina layer during cyclic



**Fig. 4** Thermogravimetric oxidation treatment of the austenitic and aluminium-containing ferritic steels showing the weight gain due to surface oxidation, as a function of time at various temperatures up to 1200°C

temperature operation. It is essential for the formation of a satisfactory bond between the substrate and the washcoat that a satisfactory key is provided on the substrate. The oxidation of Fecralloy steel and some other aluminium-containing ferritic steels provides an alumina-rich surface which is adherent and self-healing. The surface oxide also provides an excellent key for washcoat application.

Adhesion tests of the alumina coating, conducted by thermally cycling strips of the steel between 200 and 1000°C at 15 second intervals for 50 cycles, revealed that coating losses averaged around 2 per cent of the total alumina coating. Measurement of the catalytic



**Fig. 5** Endurance tests of ceramic and metal substrate catalysts used for control of carbon monoxide (CO) and hydrocarbon (HC) emissions from automobile exhaust. The emissions are shown as a function of mileage accumulation.

- 4 inches diameter × 6 inches long  
platinised metal catalyst without an  
alumina layer
- 4 inches diameter × 6 inches long  
ceramic substrate catalyst
- ×—4 inches diameter × 3 inches long  
metal substrate catalyst

alumina surface area after high temperature firing (1100°C for 2 hours) showed that it retained its high surface area (80 m<sup>2</sup>/g), necessary for high temperature stability of the catalyst in emission control applications.

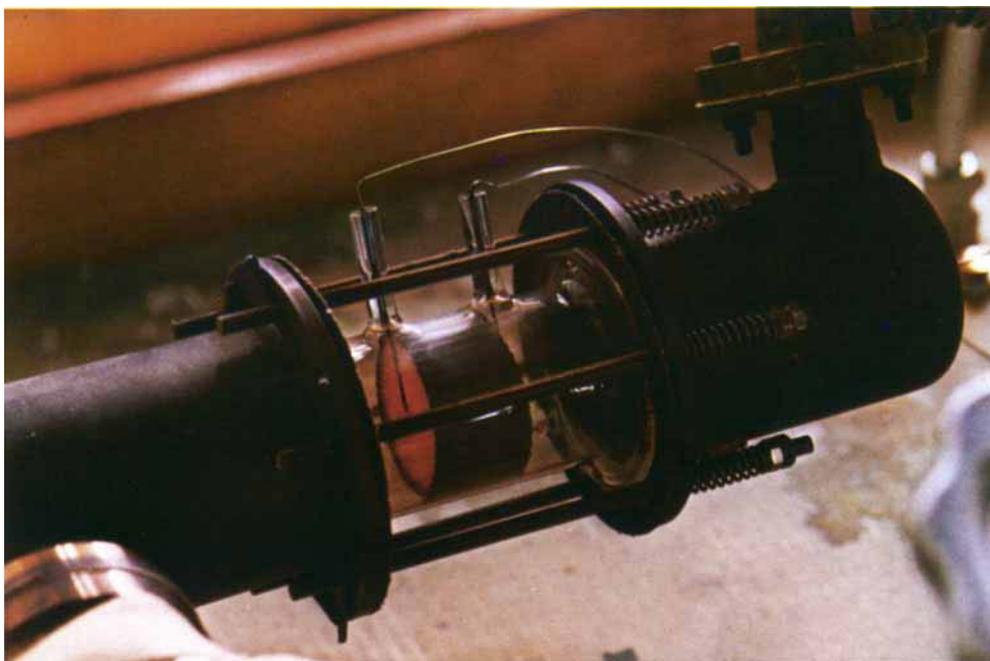
This alumina has the additional advantage that it is fully compatible with existing monolith catalyst production plant (9), allowing the interchange of ceramic and metal substrate catalyst manufacture. Comparative tests of ceramic and metal monolith catalysts, to establish adhesion of the catalytic alumina layer, were carried out by the following procedures: (a) a multiple water wash, (b) a high pressure air jet attrition test and (c) a thermal shock test where the monolith is subjected to 20 temperature cycles between ambient and 650 to 850°C. The results (Table II) show that excellent adhesion, comparable to the ceramic monolith currently used in automotive emission control applications, is obtained with the metal substrate.

Application of the platinum group metals to the surface of the metal substrate is carried out by proprietary techniques, but again the methods used are fully compatible with existing production plant.

### Emission Control Using Catalysts on Metallic Substrates

Catalysts on metallic substrates have been evaluated against two primary emission control applications, namely automobile emission control and catalytic combustion. In the former process the catalyst is installed in the exhaust train to treat the emission from the combustion chamber. An illustration of the environment is shown in Figure 6. The principles of this method have been reviewed previously in this journal (5, 10, 11, 12). In the latter process the catalyst is installed in the combustion chamber and the air/fuel mixture burnt catalytically over the active platinum surface. Hence catalytic combustion possesses the major advantage of lower NO<sub>x</sub> emission due to lower combustion temperatures preventing fixation of nitrogen. This method of emission control is currently being actively researched (13-16) for gas turbine engines, where the continuous combustion process is directly amenable to catalytic treatment.

Endurance tests made on metal substrate



*Fig. 6 Preliminary evaluation of metal substrate catalysts for automobile emission control applications were undertaken with units installed in the exhaust system of a single cylinder 4-stroke 50cc engine. On combustion the exhaust gas emitted generates a high temperature close to the catalyst, as is shown in the photograph where a unit is seen temporarily working in a silica holder*

catalysts used for carbon monoxide and hydro-carbon emission control from automobile exhaust have shown that the catalytic durability of the metal supported catalyst is equal to or greater than its ceramic counterpart. Emission tests conducted over the U.S. Federal emission test procedure have also confirmed the original predictions that the metal substrate catalyst is capable of achieving similar emissions to the ceramic catalyst using half the ceramic volume (Figure 5). Fecralloy steel substrate catalysts have been tested over 50,000 miles (Figure 7) and have met Federal statutory limits. Metal substrates are also compatible with "Three Way Catalyst" (11) formulations, used for simultaneous control of carbon monoxide, hydro-carbon and nitro-

gen-oxide emissions from automobile exhaust (Table III).

The particular advantages of the metal substrate are again apparent in the use of catalysts to promote combustion in the gas

<b>Table II</b> <b>Comparison of the Adhesion of the Catalytic Alumina Coating to Metal and Ceramic Substrates by Water Washing, Air Attrition and Thermal Shock Tests</b>				
Sub- strate	Alumina Loss per cent			
	Multiple Water Wash	Air Attrition	Thermal Shock 650°C 850°C	
Metal	0	0	1.8	2.4
Ceramic	0	<0.5	1.8	3.6

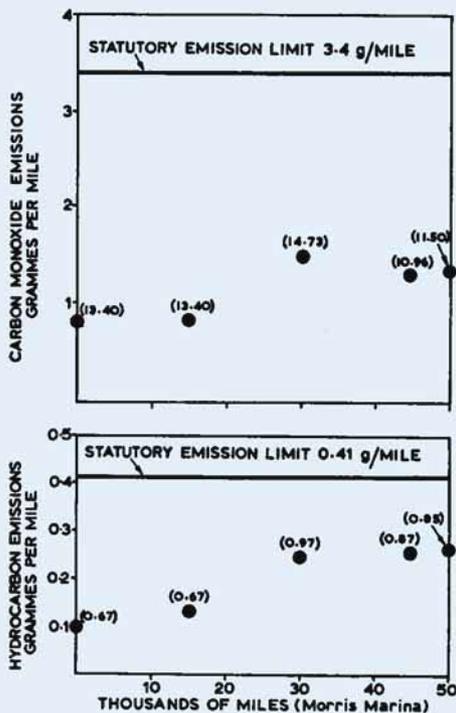


Fig. 7 Metal substrate catalysts have been tested for emission control over distances up to 50,000 miles and all the results are well below the Federal limits. The numbers in parenthesis show the engine emissions in the absence of a catalyst

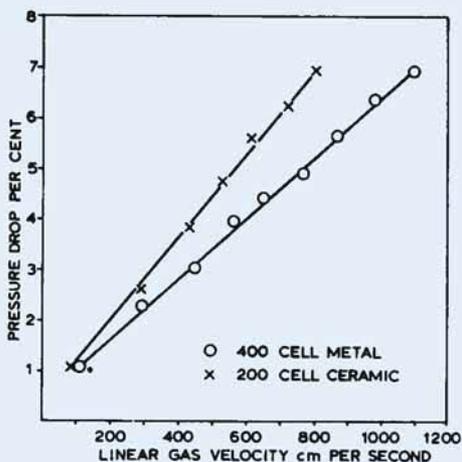


Fig. 8 Comparison of the pressure drop across 2 inches diameter  $\times$  3 inches long metal and ceramic substrate catalyst beds

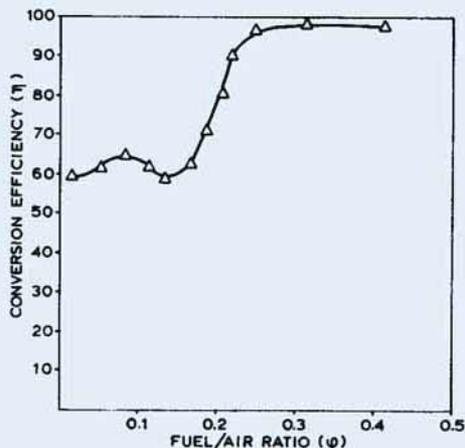


Fig. 9 Conversion efficiency of a metal substrate catalyst as a function of the fuel to air ratio, in the combustion of kerosene. Operating conditions 40 psi,  $1.25 \times 10^6$  space velocity per hour, 30 cm sample

turbine engine. In this context the low pressure drop of the metal substrate catalyst (Figure 8) gives the added advantage that catalytic combustors may be designed with minimal power loss, while at the same time achieving high combustion efficiency (Figure 9). Measurement of  $\text{NO}_x$  emissions from the catalytic combustor operating under conditions typical of a gas turbine engine showed the emission to be less than 25 ppm, which compares with 100 to 500 ppm for the conventional gas phase flame combustor.

## Conclusions

Research in the Johnson Matthey and Harwell Laboratories has led to the development of a durable platinum group metal catalyst bonded to an aluminium-containing ferritic steel. Fabrication of the steel substrate into a cellular monolith structure gives a compact and efficient catalyst system free of the thermal and mechanical failure problems associated with similar ceramic structures. Metal substrate catalysts are particularly applicable to high flow, high temperature environments typical of those in automobile emission control and catalytic combustion.

Table III Comparison of the Conversion Efficiency of Metal and Ceramic Substrate "Three Way Catalysts" During a 300 hour Endurance Test												
	Hydrocarbon				Carbon Monoxide				Nitrogen Oxide			
	Test Hours				Test Hours				Test Hours			
	0	100	200	300	0	100	200	300	0	100	200	300
Metal Substrate 6 inches dia. × 4 inches	82	75	80	73	80	84	88	83	98	84	79	80
Ceramic Substrate 6 inches dia. × 4 inches	78	81	70	74	88	87	86	78	67	65	61	63

Conventional gas phase combustors inject fuel into the combustion chamber in the form of droplets. Combustion occurs on the droplet surface at stoichiometric air/fuel ratio giving rise to high local flame temperatures and leading to the formation of NO<sub>x</sub>. Attempts to overcome NO<sub>x</sub> formation by prevapourising the fuel to give a lean homogeneous fuel/air mixture, and hence lower peak combustion temperatures, are fraught with difficulty due to limitation of flame stability under weak fuel/air operation.

Catalytic combustion possesses the major advantage that the combustion process is not subject to the lean flame stability limitation of gas phase combustion. Tests on a Johnson Matthey metal substrate catalyst system have recently been reported by Exxon (16).

#### Acknowledgements

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