Association of Indian Automobile Manufacturers

Metallic Substrates for Catalysts in Passenger Cars, Two and Three Wheelers

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Seminar: „Catalytic Converters : Fresh Steps“
20th & 21th February 1995 at Bangalore, India
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1 Abstract

Metallic substrates constitute a supporting technology to meet the world wide stringent emission legislations for passenger cars as well as for two and three wheelers. Low data of thermal capacity lead to an early light off. High thermal conductivity helps the catalyst under engine misfiring conditions. The wall thickness of the used foil material is responsible for low backpressure and high engine performance.

Structurized surfaces (Transversal Structure) and Electrically Heated Catalysts are the basis for the most favourable possible results in exhaust emissions. The larger geometrical surface area of metallic substrates in combination with the Transversal Structure offers the industry a 30% reduction in catalyst volume as well as in the costs of precious metals. Simple and cost saving canning methods are a field of special interest in the motorbike industry.

To gain benefit from the properties of metallic substrates it is essential to find an appropriate engineering solution.

2 Introduction

According to worldwide increase of emission limitations there is a demand for new and innovative technologies in the field of substrates and coatings for catalytic converters. The guidelines for the technical requirements are defined in the United States with TLEV, LEV and ULEV Standards. Based on this Europe, South America and many Asian countries have decided more stringent emission legislations. The Indian Government is introducing tight emission norms for implementation in 1996 and goals for 2001. Even though there are different drive cycles in the different countries and regions, there are at least similar requirements for catalysts such as improved mechanical durability, emission stability, early light off and minimal installation space. Metallic substrates possess a number of properties which support the requirements of the car and the motorbike industries. This type of substrate, therefore, could gain soon an increasing market share within a short period of time after the basic metallurgical, design and production development have been successfully completed.
3 History of metallic substrates

The first but unsuccessful research was carried out on metallic substrates in the early sixties in the United States. Flat and corrugated metal foils were combined and wound to a spiral formed body (see Fig 1). Because there was no technology available to fix the foils to each other and to the outer mantle, the parts failed under testing. The fixation of the matrix in the outer housing was solved in 1978, when an appropriate brazing technology was devised by our group.

Brazed spiral type metal substrates showed problems in application tests and in the field, which made it necessary to find an answer for creep fatigue phenomena. This was achieved in 1986, when the so-called S-Design substrate was introduced to the market. For applications under very high loads another design, designated the SM Design was introduced. At temperatures > 900 °C and accelerations > 80 g, which can be found in two wheelers, this design showed the required mechanical durability.

![Fig. 1 History of metallic substrates](image)

3.1 Material

The material and its treatment in the production process are important factors for durability. Metallic substrates are made with a foil of about 40 µm thickness. This foil must be mechanically durable and corrosion-resistant against exhaust gases over the lifetime of the vehicle. The material used for this is an IRON-CHROMIUM-ALUMINIUM-alloy, which is given a special surface treatment within the production process to build up a layer to protect the material against oxidation. Furthermore, the surface layer is important for achieving good wash coat adhesion after the coating procedure. In /1/ and /2/ it was reported, that test data on metallic substrates give the same respectively slightly better wash coat adhesion results than on ceramic substrates.

3.2 Metallic and Ceramic Substrates Data

Metal substrates can be made with the same foil thickness of about 40 µm for cell densities of 25 to 600 which provides the flexibility to optimize for maximum catalytic or power performance. The main differences between standard ceramic substrates and standard metallic substrates are given in Fig 2. The comparison is made under the assumption that both substrates have a cell density of 400 cpsi. All data are given for uncoated substrates. Due to the fact, that the wall thickness of metallic substrates is just 25 % of a ceramic substrate, there is a higher clear cross section in metal substrates. This leads to a significant decrease in backpressure which gives a higher performance to the engine and a reduced fuel consumption. Based on the thin walls and the different cell structure, metal substrates show a higher geometrical surface area than ceramics. It will be shown later on, that geometrical surface area is one of the important factors to influence the emission results.

![Fig. 2 Comparison of Data of Metal and Ceramic Supports](image)

<table>
<thead>
<tr>
<th></th>
<th>Metal</th>
<th>Ceramic</th>
<th>Thin Wall Ceramic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wall thickness (mm) (mil)</td>
<td>0.04</td>
<td>0.16</td>
<td>0.14 (0.13)</td>
</tr>
<tr>
<td>Cell density (cpsi)</td>
<td>400 (50-600)</td>
<td>400</td>
<td>350 (470)</td>
</tr>
<tr>
<td>Clear cross section (%)</td>
<td>91.4</td>
<td>76.0</td>
<td>80.5 (79.5)</td>
</tr>
<tr>
<td>Geometrical surface (m²/l)</td>
<td>3.7</td>
<td>2.8</td>
<td>2.8 (3.03)</td>
</tr>
<tr>
<td>Specific heat capacity material (kJ/kgK)</td>
<td>0.5</td>
<td>1.1</td>
<td>1.1 (1.1)</td>
</tr>
<tr>
<td>Specific heat capacity (J/kgK)</td>
<td>301</td>
<td>451</td>
<td>440 (451)</td>
</tr>
<tr>
<td>Thermal conductivity (W/mK)</td>
<td>14</td>
<td>1</td>
<td>1 (1)</td>
</tr>
</tbody>
</table>

The specific heat of the metal material is about 50 % that of ceramics. Taking into account, that the metal foil has a higher specific density and the ceramic substrate has a higher wall thickness, there is a remaining advantage for metal substrates of 150 J/kgK. Considering that metal substrates can work with smaller volumes, the thermal mass of metallic substrates will decrease further. Thermal conductivity of metal substrates is higher. This helps to prevent to damage the substrates in case of irregular engine function such as misfiring. Local heat can be conducted to the adjacent structures. This is important for high exothermal temperature peaks which will cause loads especially in close coupled and two stroke applications.

3.2.1 Mechanical Durability and S Design

In the 80s the car industry showed increasing interest in using metal substrates for close coupled applications. In this position they were exposed to extreme high temperature transients and gradients. As a result the thermal expansion behaviour of the thin foil and the thicker mantle housing causes high thermal and mechanical loads. Additionally, the engine vibrations and flow pulsations increase the load level. Since the metal honeycomb must be securely attached to the mantle, but at the same time a high amount of elasticity
for the bonded structures must be achieved to avoid creep fatigue defects. Emitec introduced in 1986 the S Design structure. To describe the difference between Spiral and S Design with the means of Finite Element Simulation, it was assumed that a 100 mm diameter substrate has at its centre a 250 °C higher temperature than at the mantle (Fig 3 + 4). This gives on both types of substrates the same deformation of the matrix of 0.073 mm. Fig 5 shows that the spiral type must bear all the deformation stress in the outer layers whereas the S-Design transfers the deformation torsionally to the centre of the matrix. A typical result according to this failing mechanism for a spiral type is given in Fig 6. Practical measurement showed, that the S Design has a mechanical durability more than 5 times higher than the spiral type.

Fig 3  Radial displacements, Spiral-type

Fig 4  Radial displacements, S-type

Fig 5  Comparison of radial displacements

4. Back Pressure

The back pressure of a catalyst is mainly influenced by the clear cross section which is available for the exhaust gas. This is a function of the wall thickness of the substrate and the thickness of the washcoat. Because of similarity of the process the wash coat on metallic and ceramic substrates can be applied with the same thickness. This leaves the thickness of the substrate walls as the determining factor. Fig 7 demonstrates the difference between back pressure for a ceramic and for a metallic catalyst. Both catalysts were coated with a similar wash coat and had identical geometrical specifications. Fig 8 shows the influence of cell density for different metallic substrates /3/.

Fig 6  Matrix Detachment after End of Life Test

Fig 7  Pressure Drop Comparison Construction similar Ceramic and Metallic Catalyst

A reduction in back pressure can be used to increase engine performance. It was found /4/ that the replacement of a ceramic catalyst by a metallic catalyst (Fig 9) with similar geometrical specifications led to a performance improvement of up to 4 kW for a high performance car. To benefit from the use of metallic substrates, appropriate
5.1 Geometrical Surface Area (GSA)

Based on the chemical parameters of catalytic performance GSA, space velocity and the catalytic agents are responsible for the conversion efficiency; this has been confirmed in a number of publications /5/6/7/. In /7/ an existing ceramic catalyst was replaced by a metal substrate with the same diameter but shortened by 18%. The conversion rates for all pollutants were slightly better after ageing (Fig 10). Fig 11 gives a comparison between coated metal and ceramic substrates over the cell densities. To achieve the adequate GSA of a 400 cps metal catalyst it is necessary to install the same volume of ceramic with 625 cps.

5. Emission Results on Metallic Substrates

Metal substrates will influence conversion efficiency by optimizing the following parameters, which partly influence each other:

- Geometrical Surface Area
  - Volume, geometrical specification
  - Cell density
- Thermal mass
- Flow distribution
- Cross section
- Location of the catalyst (underfloor or close coupled).

5.2 Light Off Behaviour

5.2.1 Influence of Heat Capacity

The material data for metal show, that metal substrates have an earlier light off than ceramic. Fig 12 shows the
difference. Metal substrates have a geometrical surface area which is higher than ceramic. This means the wash coat mass on metallic catalysts is higher, which reduces the difference in thermal capacity between metal and ceramic more than expected. For practical application this means, that a 1:1 volume comparison should be considered, for example, with a lower cell density or a reduced volume for metal. Metal substrates offer the same conversion with about 20% less volume.

![Graph showing Heat Capacity vs Cell Density for Metal and Ceramic Catalysts](image)

Fig. 12 Physical Data Metal/Ceramic-Catalyst, Heat Capacity; Coating Thickness 0.025 mm

### 5.2.2 Influence of Diameter on Light Off

This parameter goes hand in hand with the influence of the heat capacity of catalyst substrates. If the available thermal energy is concentrated in a smaller volume, the consequence is an earlier light off for the smallest diameter as to be seen in a computer simulation (Fig 13). In any case the diameter can be reduced compared to ceramic utilizing the back pressure benefit of metallic substrates.

![Graph showing HC Conversion Rate vs Time for different diameters](image)

Fig. 13 Catalyst Calculation over FTP, Bag 1

### 5.2.3 Influence of Cell Density on Light Off

The location of the catalyst has an important influence on the layout of the catalyst. In the underfloor the design must be different than in a close coupled position. Fig 14 shows, that the dominating factor is the gas intake temperature /\T/\. The test work was carried out with ceramic substrates which were exposed to exhaust gas heated to 600 K and 700 K respectively. This simulates an underfloor and a close coupled position.

For 600 K the 200 cpsi catalyst shows the earliest light off, whereas the 600 cpsi catalyst shows the worst results. In this position the thermal capacity of the catalyst is the dominating factor. For 700 K the opposite result was found. The catalyst with 600 cpsi has the earliest light off. In this simulated close coupled position where enough thermal energy is available, the geometrical surface area of the catalyst is the dominating factor. Depending on the location of the catalyst a compromise between the factors specific heat and GSA might be the best solution for long term emission durability.

Another example for the influence of cell density is given in Fig 15 for an underfloor application. For metal catalysts with two different cell densities and ceramic catalysts with appr. identical volumes, a detailed analysis of Bag 1 in the FTP was carried out /\9/. The 300 cpsi metal catalyst with the lowest thermal capacity has the highest HC conversion rate in the first 150 sec. The 400 cpsi metal catalyst has still a smaller thermal capacity than the ceramic catalyst which leads to a higher HC conversion rate. The time between 150 and 505 sec shows a small advantage for the 400 cpsi metal catalyst which is explained by the higher geometrical surface.

![Graph showing CO Conversion vs Time for different cell densities](image)

Fig. 14 Influence of Temp. and Cell-Density on Light off Behaviour; Gastemperature in front of Catalyst at 600 K resp. 700 K
5.3 Design Criteria for Close Coupled Catalysts

Various catalyst sizes were tested in a first development step on a 1.8 l engine. All samples had a coating of 50 g ft⁻¹. Fig 16 describes the behaviour of the catalysts. Bag one was divided in a first part from 0 - 125 seconds and a second part from 126 - 505 seconds. In the time between 0 - 125 seconds it can be seen, that the catalyst with Ø 90 x 74.5 mm, 400 cps values gives the optimal compromise between thermal mass and GSA. Smaller catalysts have too small GSA, and at larger catalysts present too great thermal mass. In the second part 126 - 505 seconds the dominating factor is GSA. Based on this result the catalyst 90 x 74.5 mm was favored for the further examinations to determine the optimal cell density. The results were obtained for cell densities from 100 cps up to 600 cps (Fig 17). The first 125 seconds show, that the GSA is still dominant. With increasing cell density the emission results are improved.

5.4 Heat Cascades

The use of heat cascades might be an advantage in the close coupled as well as in the underfloor position. But in close coupled application there is normally enough thermal energy available for an early light off. Therefore the highest improvement with heat cascades can be expected in the underfloor position. A first catalyst with a low thermal mass must come to an early light off and create enough thermal enthalpy to light off the following system. The two described applications were both located in the underfloor.

**Fig. 15 HC Conversion Rates versus time over FTP, Bag 1**

**Fig. 16 Influence of Catalyst Diameter on HC-Conversion Rate in FTP (fresh)**

**Fig. 17 Influence of Cell Density on HC Conversion Rate in FTP Bag**

**Fig. 18 Comparison Metal Heat Cascade vs Ceramic Converter**

In Fig 18 a ceramic race track system was compared with a round metallic heat cascade over the FTP, Bag 1.
The mid bed temperatures for both systems indicate that the smaller metal substrate with a reduced cell density shows light off after 60 seconds whereas the ceramic race track needs 90 seconds. The first metal substrate is followed by a larger metallic substrate with a cell density of 300 and TS-Structure. The complete metallic heat cascade system is 90 seconds earlier at operation temperature than the ceramic system. The emission data for the metallic catalyst which was 0.3 ltr. smaller in volume offers the potential improvement of heat cascades. In Fig. 19 it is shown how a metallic system can be improved by means of heat cascades. Furthermore it was examined if there is a different influence on FTP or ECE-results. The production converter tailpipe emissions were put to 100%. Using different cell densities for the first catalyst of the heat cascade the result was obtained that 100 cpsi is the best compromise between thermal mass and GSA in this application.

6. Transversal Structure

It was shown, that metallic substrates can work with approximately 20% less volume, because they offer more GSA to the exhaust gas. Metal substrates offer potential for a further reduction in volume of approx. 10% by using a structurized surface known as Transversal Structure (TS). The corrugated and flat foils are embossed with a secondary corrugation. Coaters are familiar with the request to work with the right wash coat viscosity in order to maintain the structured profile after coating (Fig. 20).

Fig. 20 Transversal Structure (TS)

About 5 - 10 mm after entrance of the exhaust gas into the channel the exhaust flow becomes laminar. As a result there is a limited exchange of energy and mass at the surface of the channel. Structuring the surface of a catalyst channel creates an increase in back pressure which is shown in Fig. 21. Between normal structured and TS Structure a difference of approximately 10% can be measured. Because a catalyst with a cell density of 300 TS cpsi has about the same conversion efficiency as a catalyst with 400 cpsi, the apparent disadvantage in back pressure becomes an advantage /10/.

In tests it was found that TS-Structure simulates 10% more conversion efficiency. Based on these data, TS Structure can be of benefit in two ways:

1. The cell density of the catalyst can be reduced and the volume remains unchanged, which gains power and reduces fuel consumption.
2. The cell density remains the same and the catalyst volume can be reduced by approx. 10%. Because the precious metal loading can remain at the same figure per volume, this becomes the most cost-effective method to implement TS Structure.
Fig. 22 represents the first method with a detailed analysis of the emissions of all 3 bags of the FTP. Fig. 23 indicates how a production catalyst of 118 x 174 mm, 400 cpsi can be replaced by a catalyst 118 x 150 mm, 400 cpsi. Both examples actually show a slightly improved emission result which indicates the greater potential of TS Structure.

7. Electrically Heated Catalysts (EHC)

In the USA and Japan the trend can be noticed towards positioning the converter in closer position to the engine rather than in the underfloor position which is unfavourable for the cold start. Whether through this measure alone, "clean" engines can fulfill LEV, EURO 2000 or even ULEV standards remains to be seen.

Dependent on the heat range in front of the converter, the engine-out emission, the position of the catalyst and the catalyst mass, the change to active heating will be necessary. EHC’s are able to improve the cold start behaviour significantly and they are considered to be a promising solution for mass production from 1998 onwards. The target of the EHC-development work was to make EHC’s mechanically durable and to reduce power consumption drastically. The development started with a power consumption of > 300 Amp/12 V which required special or second batteries and high-performance power switches. Today’s status is, that EHC’s are available with 35 Amp/12 V. The design of this development is given in Fig. 24. The necessary power consumption is dependant on the location of the EHC. Average figures for engines with less than 2.0 l. displacement are between 80 Amps and 150 Amps. The efficiency over the first 125 seconds of an EHC is shown in Fig. 25. Reduction in heat loss, modification of engine management parameters and optimization of secondary air injection are further criteria to achieve ULEV standard.
8 Canning Methods and Requirements

Metallic substrates consist of a metallic matrix and an outer mantle which is made either from ferritic or austenitic steel. This mantle is already a part of the canning and in many applications it is sufficient to provide the metallic catalyst with the inlet and the outlet cone. In order to avoid predamaging the substrate, the welding between mantle and cone should be a distance of approximately 5 mm from the matrix. Fig 26 gives an example, how to can metal substrates in the right way. Particularly in motorbikes the use of metallic substrates is advantageous. Integrating the catalyst into the muffler is a simple, cost saving and efficient way of canning (Fig 27).

9 Test Methods for Product Qualification

To avoid any problems with metallic substrates in the field it is necessary to expose them to defined loadings; these are covered by the following standard tests /12/:

- Exhaust Emission Simulator Tests
  - Inner Thermal Cycling Test (ITC)
  - Hot Shake Test (HST)
  - Outer Thermal Cycling Test (OTC)
- Engine Thermal Cycling Test (ETC)
- Electrical Inner Thermal Cycling Test (EITC)
- Vehicle Durability Test

10 Recycling

The industry requires recycling of catalysts to recover the precious metal as well as other materials. Metal substrates can be recycled by a simple process (Fig 28). The complete converter is granulated in a shredder, where the matrix material is separated from the mantle material. Ferritic matrix material and austenitic mantle material are separated by a magnet and returned to the circuit /13/.

In the shredder process the precious metal containing washcoat peels off from the matrix and is collected in a cyclone. In chemical and metallurgical processes it is possible to recover appr. 95 % of the Platinum and appr. 80 % of the Rhodium /14/.

Fig. 25 Catalys Calculation, Cumulated HC-Emissions of a 2,0 ltr Turbo, 4 valve engine over FTP

Fig. 26 Canning Requirements for Metallic Substrates

Fig. 27 Integration of Metallic Catalyst into the Muffler of a Motor Bike

Fig. 28 Recycling
11 Summary and Conclusions

The results presented describe the current status of metallic substrate development. They indicate that metallic substrates can provide the technical properties necessary to conform with both current and future legislation, particularly with regard to durability, light off and space requirements. In the short time they have been available to the industry in the required quality, metallic substrates have gained a significant share of the market. Looking to worldwide activities in the application of catalytic converters, a continuation of this trend can be seen, resulting from the introduction of more stringent emission legislation. Physical, mechanical and geometrical properties of metallic substrates constitute parameters which can only be of benefit in support of new legislation.

References: