Abstract

Stringent emissions regulations for the exhaust gas of motor vehicles are in place worldwide. It is a significant challenge to develop advanced exhaust gas after-treatment systems in order to meet such stringent emission standards. Improvements of purification capability and durability of metal substrates are expected by applying new technologies to gas flow channel structure or to surface condition improvement of the stainless foil. In this study, we propose an ‘offset substrate’ with a structure of periodical wall shifting of exhaust gas flow channels in the gas flow direction, which showed effectiveness for increasing the purification efficiency especially for high exhaust gas flow rate. Also, ‘α film coated substrate’, which has a special oxide film on the surface of the stainless foil formed by heat treatment in an oxidation atmosphere at high temperature, showed an excellent acid corrosion resistance and accessibility to the anticipated corrosive environment in the SCR system. These advanced metal substrates are expected to be important key items for compliance with the stringent emissions regulations.

1. Introduction

The exhaust gas from two-wheeled motorcycles and four-wheeled vehicles contains hazardous components such as CO, HC and NO\textsubscript{x}, and such components are detoxified through the oxidation or reduction reaction by catalysts of precious metals such as Pt, Pd and Rh. These catalysts are supported on a honeycomb type substrate to ensure effective contact with the exhaust gas. The honeycomb substrate with the catalyst is installed in the exhaust gas pipe and is used for purifying the exhaust gas. Ceramic substrates made of extruded cordierite, or metal substrates made of stainless steel (SUS) foil 20–100 \(\mu\)m thick are used as honeycomb substrates. A flat sheet and a corrugated sheet are wound around, and are brazed to form the metal substrate. Nippon Steel & Sumikin Materials Co., Ltd. has developed and has been supplying a metal substrate with a gate-shaped brazing structure having excellent heat cycle durability, which is constructed of ferritic SUS foil containing high Al content, and having excellent high temperature oxidation resistance.\(^{2-5}\)

Emission regulations for the exhaust gas of motor vehicles are growing increasingly stringent year by year. In Europe, in particular, the RDE (Real Driving Emission) regulation, a regulation that regulates the emissions of exhaust gas under actual driving conditions, is scheduled to be introduced in 2017\(^{6}\) in addition to the conventional regulations based on the driving cycle under a constant driving condition. Meanwhile, regulations on fuel consumption are also promoted, and to comply with these regulations, developments to improve combustion in engines and exhaust gas after-treatment systems are being promoted.\(^{7,8}\)

Precious metals used for catalysts are costly, and the reduction in the use of the precious metal is required. To realize the requirements, in addition to improving the catalyst performance, technologies to control the heat and the flow of exhaust gas in a honeycomb substrate are required to improve the purification performance.

To date, Nippon Steel & Sumikin Materials has developed a substrate composed of SUS foil perforated with micro holes of less than 1 mm in diameter, and proposed improvement in the light-off performance of the catalyst at the cold start by reducing the heat ca-
pacity. The substrate was mounted on cars in the market. As various spatial structures can be formed by a process such as press-working with specifically designed dies on the SUS foil that constitutes a substrate, a substrate having a spatial structure effective in improving the purification performance is proposed. To date, protrusions with a height of several hundred μm were provided on the corrugated sheet, and the structure with the corrugated sheet turned upside down has been proposed. Structures to improve the conversion efficiency by further increasing the chance of the contact of the exhaust gas molecules with a catalyst are required. Therefore, the offset structure with a channel-shifted corrugated sheet as shown in Fig. 1 was proposed, and remarkable improvement in the conversion efficiency as compared with that of the conventional structure was confirmed.

Furthermore, in the after-treatment system of selective catalytic reduction (SCR) by urea for diesel engine vehicles, exhaust gas is reduced (SCR) by urea for diesel engine vehicles, exhaust gas is on the interaction between the exhaust gas and the catalyst. The reaction rate is expressed by the following equation: 

\[ \text{rate} = \text{rate}_0 \times \exp(-\frac{\Delta H}{RT}) \times \text{rate}_d \]

where \( \Delta H \) is the activation energy, \( R \) is the gas constant, \( T \) is the temperature, and \( \text{rate}_d \) is the rate of the diffusion of reactants to the catalyst. The rate of the catalytic reaction can be expressed as a function of the concentration of the reactants, but it can also be expressed as a function of the diffusion rate of the reactants. Therefore, gas diffusion is considered to be enhanced.

Figure 1 shows the exhaust gas flow through the conventional substrate structure and that through the OS substrate structure schematically. In the conventional structure, the exhaust gas flow changes to laminar flow from turbulent flow at a distance several millimeters away from the inlet section. The laminar flow is maintained afterwards in the gas channel.

The catalytic reaction takes place on the catalyst coated on the channel wall. In the laminar flow, the mass transfer to the catalyst in the channel is carried out only by the diffusion of the molecule. Accordingly, the higher the reaction velocity in the catalyst layer becomes, the lower the concentrations of the reactants such as CO, HC and NO\(_x\) in the vicinity of the catalyst layer become. However, the mass transfer of the reactants from the center section of the channel to the catalyst layer cannot maintain pace with the reaction rate. Therefore, the catalytic reaction is controlled by the diffusion under the condition that the concentrations of the reactants are high in the center section. This means contrarily that the conversion efficiency can be improved if the mass transfer of the gas components is enhanced.

In the OS structure, the wall of the channel coated with a catalyst is positioned at the center of the incoming flow at its offset position. Even though the concentrations of the reactants such as CO, HC and NO\(_x\) remain high in the center section of the laminar flow region, it is considered that the reactants come into contact with the catalyst at the offset position, and conversion is carried out efficiently. Furthermore, at the offset position, the gas reactants collide with the offset channel wall and the laminar flow becomes turbulent. Therefore, gas diffusion is considered to be enhanced.

The OS structure is considered to be effective in the region with a relatively high conversion rate wherein the diffusion of the reactants controls the conversion rate. Figure 2 shows the effect of the OS structure on the purification performance schematically using the relationship between the gas temperature and the conversion rate. As the exhaust gas temperature rises, the catalyst is more activated and the conversion rate increases. In the region wherein the gas temperature is lower and the conversion rate is below 50%, and the catalytic reaction rate controls the conversion rate, the mass transfer does not control the conversion rate. The effect of the OS structure is expected in the region above 50% of the conversion rate wherein the diffusion controls the conversion rate, and the conversion rate higher than that obtained by the conventional structure is obtained at the same temperature. Particularly, under the condition of high flow rate (high SV: high space velocity) in high load and high speed of the revolution of engines, the diffusion of the reactants to the catalyst layer is insufficient and the reactants of exhaust...
gas tend to pass through the substrate. Therefore, the OS structure is considered to be effective and the SV toughness (rate of increase in SV vs. corresponding deterioration of conversion rate) is considered excellent.

2.2 Verification of effect of OS structure by computer simulation

The CO concentration distributions developed by the CO oxidation reaction in the gas flow in the OS structure provided with the offset channel and that in the conventional structure, and their changes in the gas flow direction were simulated and compared. The simulation software used was FIDAP.

Figure 4 shows the contour map of the CO concentration distribution on a plane perpendicular to the direction of the gas flow at 5 mm intervals. The SV value used for the calculation was 90,000 h⁻¹. In the case of the conventional structure (200 cpi (cells per square inch), channel length: 50 mm), although the CO concentration was uniformly distributed in the inlet section, in the section 5 mm apart from the inlet section, the CO concentration exhibited the distribution of lower CO concentration on the channel wall sides (catalyst layer sides) than that in the center section of the channel. The CO concentration continued to decrease in the direction of the gas flow, maintaining this pattern of distribution. In the case of the OS structure (200 cpi, channel length: 50 mm, OS pitch: 5 mm), the CO concentration distribution pattern remained the same as that of the conventional structure for 5 mm from the inlet section. When the CO gas with high concentration comes into contact with the channel wall (catalyst layer) offset by 5 mm pitch, the reaction rate at the point of contact becomes higher because the higher the CO concentration is, the higher the CO oxidation rate becomes. As a result, the average CO concentration became than that of the conventional structure, and at the position 50 mm away from the inlet, the difference in CO conversion rate increased to about 5%.

3. Development of Offset Substrate (OS)

3.1 Experiment method

(1) Trial manufacturing of OS substrate

A corrugated sheet provided with the OS structure was manufactured by press-forming, using the SUS foil of 20Cr-5Al steel (YUS 205M1, sheet thickness 50 μm). Subsequently, an OS substrate was trial-manufactured by laying a flat sheet on the corrugated sheet and by brazing them at some of the contact parts.

Figure 5 shows a schematic drawing of the corrugated sheet provided with the OS structure. Each cell is of trapezoid shape, and measures a mm in width, b mm in cell height. The OS pitch is c mm. In Table 1, the specification of each OS substrate that was trial-manufactured in this research is shown. The cell density was varied in the range from 150 cpi to 625 cpi, and the aspect ratio b/a of the cell shape was varied in the range from 1 to 4. For comparison purposes, conventional metal substrates were trial-manufactured, using the same SUS foil. The cell was of triangular wave shape and the cell density was varied in the range from 100 cpi to 600 cpi.
(2) Supporting catalyst

The catalyst supported by each substrate is a three-way catalyst of Pd as precious metals. The specified quantities of complex oxide powder of CeO$_2$-ZrO$_2$, gamma Al$_2$O$_3$ powder, and Palladium nitride acid aqueous solution were mixed. Then the water was evaporated in a vacuum evaporator and catalyst powder with Pd was prepared. The powder was calcined in air at 550°C for 5 h, and Pd was fixed on the complex oxide. Specified quantities of the Pd-containing powder and a binder were mixed in water to produce wash coat slurry, and the catalyst was coated in each substrate. The quantity of the wash coat with the catalyst is 180 g/L for the volume of the substrate, in which the amount of Pd is 2.5 g/L. To simulate thermal degradation of catalyst activity, the catalyst coated on the substrate was heated up to 980°C and maintained for 20 h in air.

Figure 6 shows the photographs of the channels of the OS substrate having the cell density of 625 cpi, the highest among the tested offset structures. The photos show the vertical sectional view, and the horizontally parallel sectional view of channels with respect to the direction of the gas flow. The photos were taken at a distance of 5 mm from the inlet section after coating a catalyst. It was confirmed that the catalyst was uniformly supported without clogging the narrow gaps of the offset channels. Therefore, in OS substrates with lower cell densities, no clogging was anticipated, and the catalyst coatability was confirmed as trouble free.

(3) Measurement of purification performance

A model gas was heated by an electric heater and was made to flow through the OS substrate, and the conversion rate vs. model gas inlet temperature was measured. The model gas contained C$_3$H$_6$, CO and NO with the stoichiometric air fuel ratio. The inlet model gas temperature was controlled by a heater and was decreased from 400°C at a rate of 3°C/min. As the temperature-decreasing rate is very small, the temperature distribution in every substrate is in a mostly steady state. Accordingly, the purification performance depends on the gas flow state in the channel without being influenced by the heat capacity of the substrate. The model gas flow rate was controlled to a specified quantity within the range from 75 000 h$^{-1}$ to

![Fig. 5 Dimensions of corrugated sheet with offset structure](image)

![Table 1 Specification of respective offset structures](image)

![Fig. 6 Photographs of offset structure (OS-625) with catalyst](image)
195000 h\(^{-1}\). The conversion rate was calculated in the following way. On a real-time basis, gases were sampled before and after the catalyst substrate and the concentrations of HC, CO, NO\(_X\) were measured. MEXA7000 of HORIBA, Ltd. was used for measuring the gas concentrations. As the effects of temperature on the changes in the conversion rates of HC, CO and NO\(_X\) were almost the same in each substrate, the conversion rate of NO\(_X\) was used for explanation in this article.

3.2 Results of experiment and study thereon

3.2.1 SV toughness of OS substrate

In both the OS substrate and the conventional metal substrate, the SV value of gas flow was increased from 75000 h\(^{-1}\) to 195000 h\(^{-1}\) that assumed a high speed driving, and the change in the NO\(_X\) conversion rate curve was investigated to study the effect in terms of SV toughness. OS substrates of cell densities of 280 cpi (OS-280) and 400 cpi (OS-400), and the metal substrate of the cell density of 400 cpi (Metal-400) were used, wherein the aspect ratios of the OS substrates are one, and the substrates measure 40 mm in width, 40 mm in height and 40 mm in length.

Figure 7 shows the pressure loss of N\(_2\) (20°C) in the respective substrate measured under the condition of 150000 h\(^{-1}\). The pressure loss in OS-280 is almost equal to that of Metal-400, and the pressure loss in OS-400 is higher than that of Metal-400 by 40%.

Figures 8, 9 show the relationships between the conversion rate of NO\(_X\) and the inlet gas temperature measured during the temperature decreasing in the cases of SVs of 75000 h\(^{-1}\) and 195000 h\(^{-1}\). In the case of SV of 75000 h\(^{-1}\), the conversion rates at 400°C were 100% in all substrates. The conversion rates start to decrease in the order of Metal-400, OS-280 and OS-400 in the temperature falling process, and this order continued to be unchanged until the conversion rate reached 20%. It was confirmed that the conversion in the substrate became more active in the order of OS-400, OS-280 and Metal-400. In the case of SV of 195000 h\(^{-1}\), although the conversion rate at 400°C could not achieve 100%, the conversion became more active in the order of OS-400, OS-280 and Metal-400 as well. In the case of SV of 195000 h\(^{-1}\), it was also confirmed that the conversion efficiency became higher in the order of OS-400, OS-280 and Metal-400, and the conversion temperature increased in all substrates as compared with the case of SV of 75000 h\(^{-1}\).

Figure 10 shows the increase of the temperature at the conversion rate of 80% in the respective substrate when SV is increased from 75000 h\(^{-1}\) to 195000 h\(^{-1}\). Increase was highest in Metal-400, and became less in the order of OS-280 and OS-400. Deterioration in the catalytic reaction became more in this order when the gas flow rate increases, and the excellent SV toughness of OS substrates was confirmed.

The pressure loss in the OS substrate of the cell density of 280 cpi was equal to that of the metal substrate of 400 cpi. However, the OS substrates are superior in catalytic activity and SV toughness. This is considered to be attributed to the following reason as pre-
dicted in the computer simulation. The catalytic reaction in the conventional metal substrate is deterred by the laminar gas flow, while in the meantime, the catalytic reaction is promoted in the OS substrate as the gas containing high concentrations of reactants comes into contact with the offset channel wall. Furthermore, when the gas flow rate increases, the contact time of the gas flow with the catalyst becomes shorter, and the conversion rate deteriorates. However, in the OS substrates, the gas flow becomes turbulent in the offset channels, the gas diffusion is promoted, and the chance of contact of the reactants with the catalyst is thereby enhanced.

3.2.2 Improvement of purification performance by flattened cell

When the cell is flattened by increasing the aspect ratio b/a of the cell dimension, the conversion activity is considered to be improved as the distance between the high concentration of reactants in laminar flow in the center of the channel and the catalyst wall can be made shorter. However, in contrast, as the increase in the pressure loss was anticipated, the optimum dimensional range was studied by evaluating the pressure loss and the conversion rate when the cell was flattened. The OS substrate selected for the study was cylindrical in form and measured 39 mm in diameter and 40 mm in height with SV of the gas flow of 100 000 h⁻¹.

Figure 11 shows the relationships between the pressure loss and the aspect ratio b/a. When the aspect ratio is 1, the pressure loss in the OS substrates of cell densities of 280 cpi and 400 cpi was equal to that of the metal substrates of cell densities of 400 cpi and 600 cpi, respectively. Even when the aspect ratio is increased to 2, the pressure loss in the OS substrates did not increase and stayed at around the same value. On the other hand, the pressure loss increased linearly as anticipated when the aspect ratio exceeded 2.

Figure 12 shows the relationships between the aspect ratio and the 80% conversion rate temperature (T80) of NOₓ. T80 of the OS substrate with the aspect ratio of 1 was lower by about 5°C than that of the conventional metal substrate that has almost equal pressure loss, and the higher conversion performance was observed. It was confirmed that when the aspect ratio increases from 1, T80 decreased monotonically and the catalytic activity grew higher as the aspect ratio becomes larger.

Concerning the above, the reason for the pressure loss being steady in the range of the aspect ratio between 1 and 2 is explained as follows. By flattening, the entire cell peripheral length increases, while the height of the cell wall that is situated in the center of the channel by offsetting decreases. It is considered that the increase of the entire cell peripheral length increases the pressure loss, while in the meantime, the decrease in the cell wall height decreases the pressure loss. It is further considered that the pressure loss is steady in the range of the aspect ratio between 1 and 2 because these two factors counteract each other. When the aspect ratio exceeds 2, the effect of the increase in the cell peripheral length becomes more influential than that of the decrease in the wall height in the channel. Then the pressure loss is considered to increase as a whole accordingly.

3.2.3 Relationships between pressure loss and conversion rate

Figure 13 shows the relationships between the pressure loss and 80% conversion rate temperature (T80) of the respective OS substrate and the conventional metal substrate. The values of the OS substrates of the aspect ratio 2 are shown (aspect ratio of OS-625 is 1). Both substrate types exhibit that the pressure loss increases as the cell density becomes higher, and T80 decreases. In the entire cell density range, T80 of the OS substrate is lower than that of the conventional metal substrate, and OS substrates have higher conversion rates, wherein the difference in T80 between the OS substrate and the conventional metal substrate is larger in the low cell density. In the low cell density substrate, the width of the channel is large and...
3.2.4 Heat cycle durability

Heat cycle durability tests were carried out for an OS substrate of gate-shaped brazing structure and a conventional metal substrate. The temperature range was 150–950°C, the heating rate was 6 500 °C per minute and the cooling rate was 4 500°C per minute. As a result, after the heat cycles of 600, neither core shift nor cell deformation was observed, and the test result satisfied the heat cycle durability criteria of Nippon Steel & Sumikin Materials. Therefore, the heat cycle durability of the OS substrate equal to or higher than that of the conventional metal substrate was confirmed.

4. Development of a film Coated Substrate

4.1 Formation of high temperature oxide film and method of evaluation

Corrosion of a metal coated with an oxide film in an aqueous solution is possibly initiated by the activation of the base metal exposed to the solution at the bottom of through defects such as pinholes and/or cracks of the coating film. This research clarifies the relationships between the through defect density of the oxide film formed on the SUS foil used for metal substrates and the oxidation treatment conditions, and proposes the optimum oxide film.

Samples of steel foils (32 μm) of 20Cr-5Al steel (YUS205M1) and 20Cr-8Al steel (YUS208) were heated at 700°C, 900°C and 1 100°C for one hour in air and were used as the test specimens. The 1M-H_2SO_4 (temperature: 25°C) deaerated by nitrogen was used as the corrosive solution. Each test specimen was soaked in the corrosive solution, and immediately, potentiodynamic anodic polarization was applied until the termination at the potential of 0.40 V.

4.2 Acid corrosion resistance of oxide film

Figure 14 shows the anodic polarization curves of oxidation-treated 20Cr-5Al steel.** In the specimen before air oxidation, and in the specimen oxidation-treated at 700°C and 1100°C, active states are observed, and the existence of through defects with exposed base metal of the foil was observed. In the specimen oxidation-treated at 900°C, cathodic current flows in the entire range of the potential, and in the vicinity of −0.4 V, a concave corresponding to the active states appeared. Furthermore, in the specimen oxidation-treated at 700°C, a loop of cathodic current appeared in the vicinity of 0−0.2 V on the lower potential side in the passive state region. These cathodic currents are considered to be produced by the reduction reaction of the FeO or Fe_2O_3 component of the oxide film and by the dissolution into the solution.

On the assumption that active dissolution takes place at the bottom of a through defect and that a hemispherical pit is formed, the defect density (area %) R is given by the following formula.**

\[ R = 0.5 \times 100 \times \frac{i_{\text{crit}}}{i_{\text{SS}}} \]

where, \( i_{\text{crit}} \): critical passivating current density, \( i_{\text{SS}} \): current density without film.

Figure 15 shows the relationships between the defect density and the oxidation temperature.** In either steel, the defect density became the lowest of (2 × 10^{-4}–3 × 10^{-5})% with the oxidation treatment temperature of 1100°C. However, the defect density scattered in a large range of 10^{-1}–10^{-3}%. The reason for scattering in the large range is considered to be attributed to the film formed at 1100°C being very fine; however, cracks are considered to be generated in the film as the film is thick. In the case of an oxidation temperature of 900°C, the defect density is 1 × 10^{-3} % and the scattering range became smaller.

The defect density of the CrN protection film produced by dry coating is 10^{-1}–10^{-2} % that is measured based on the same evaluation method.** Therefore, the defect densities of the oxide films that are oxidation-treated at 900°C and 1100°C are equal to or below that of the CrN film. Accordingly, 20Cr-5Al SUS with oxide film exhibited excellent acid corrosion resistance in the weak acidic or weak alkaline condensed solution of exhaust gas.**

4.3 Microstructure of oxide film

Figure 16 shows the TEM image of the oxide film formed on the 20Cr-5Al SUS surface by heating at 900°C for 1 h in air. The oxide film is about 200 nm thick and consisted of crystal grains 50–150 nm in size. Since it was confirmed from the result of the µ diffraction analysis of each crystal grain that the crystal grains had the...
crystalline structure of a triclinic system, and that the component elements were Al and O from the result of the analysis by energy dispersive X-ray spectrometry (EDX) analysis, the major phase that constitutes the oxide film could be identified as $\alpha$-Al$_2$O$_3$.

$\alpha$-Al$_2$O$_3$ is chemically stable and almost insoluble in acidic or alkaline solution. Therefore, the SUS foil covered with $\alpha$-Al$_2$O$_3$ with a very low defect density exhibited excellent corrosion resistance in the weak acidic or weak alkaline condensed solution of exhaust gas.

5. Conclusion

This research has shown the high possibility of a dramatic improvement of the performance of the metal substrate for exhaust gas catalytic converters by introducing new technologies to its gas channel structure and SUS foil surface. The offset substrate that employed offset channels and the flattened cell structure has achieved low pressure loss and improved purification performance. Furthermore, the substrate with the $\alpha$ alumina oxide film with very low defect density formed on the surface of the SUS foil with high Al content by oxidation at high temperatures exhibits excellent corrosion resistance in the condensed solution of exhaust gas which is anticipated to be weak acidity or weak alkalinity.

As cost performance higher than that of the conventional metal substrate is obtained with the new substrate, applications not only to the exhaust gas after-treatment systems of two-wheeled motorcycles and four-wheeled vehicles, but also to other uses such as heat exchanger are expected.

References
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