Development of Metal Catalyst Support Applying Solid Phase Diffusion Bonding

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Abstract

A new metal catalyst support by solid phase diffusion bonding method was developed. Nippon Steel has mass-produced metal catalyst supports by brazing bonding since 1990 for various models of cars. The brazing bonding method has been used for bonding conventional honeycomb materials for its strong bonding capability, but it has drawbacks such as deterioration of oxidation resistance near the bonds, solder corrosion with excessive solder and high costs. With this as a background, Nippon Steel pursued the possibility of solderless bonding methods, and developed a new metal catalyst support by a solid phase diffusion bonding method using a large vacuum furnace for the brazing bonding. Commercial application of the diffusion bonding method to the metal catalyst supports was difficult because of a strong alumina film, hindering diffusion bonding, formed on the surface of the highly heat-resistant Fe-Cr-Al stainless steel foil used for the support honeycomb. A new solid phase diffusion bonding method applicable to the catalyst supports was developed by removing the alumina film to secure stable bonding and providing good anti-oxidation properties. The catalyst supports manufactured by the developed method have been commercially used for cars since 1998.

1. Introduction

In the worldwide trend toward ever stringent regulations on car exhaust gases, the use of metal catalyst supports for cleaning exhaust gases has remarkably expanded recently thanks to their superior gas cleaning performance and mechanical durability over conventional ceramic catalyst supports. Nippon Steel began development of the metal catalyst supports in 1986 based on the brazing bonding method and commenced commercial mass-production of

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the supports in 1990[1-3]. Then, for attaining a better gas cleaning performance, the company launched metal catalyst supports with 30-μm thick honeycomb foils to the market in 1997 to replace the conventional supports with 50-μm thick foils[4]. Since then Nippon Steel's metal catalyst supports have been applied to various models of cars.

While the brazing method realizes strong bonding of the honeycomb and stable product quality, it has drawbacks such as the following: deterioration of oxidation resistance owing to low Al contents near the bonds; delicate control of brazing metal supply in appropriate quantities; and a high cost of the brazing metal. Besides the brazing bonding, mechanical bonding was applied to the fabrication of commercial metal catalyst supports, but the method could not offer a sufficient durability, though advantageous in terms of the cost.

In this context, Nippon Steel commenced development of a new high-performance and low-cost metal catalyst support without brazing, and succeeded in commercially applying the solid phase diffusion bonding technology of foils of highly heat-resistant Fe-Cr-Al stainless steel, which application had been commercially impracticable. This report describes theoretical aspects of the diffusion bonding of the Fe-Cr-Al stainless steel foils and manufacturing technologies of the metal catalyst support by the method.

2. Metal Catalyst Support Manufactured by Diffusion Bonding

Diffusion bonding is a method of binding materials by heating them to high temperatures in a high vacuum while holding them firmly in contact to each other. When manufacturing a metal catalyst support, a flat foil and a corrugated foil each about 50 μm in thickness are spirally wound into a honeycomb and contact portions of the foils are bonded by diffusion bonding. But it is impossible to accelerate the diffusion bonding by increasing the contact pressure because, owing to the small foil thickness, it is difficult to impose a large tension on the foils during the winding or a surface pressure evenly on the honeycomb body from outside. Furthermore, foils of a highly heat resistant 20Cr-5Al steel (YUS2051) are used for the catalyst support honeycomb body, and a strong alumina film forms on the surface of the foils having such a high Al content. While the alumina film makes the foils resistant against oxidation, it also acts as an obstacle to diffusion bonding. Various parties have proposed different methods to manufacture metal catalyst supports by the diffusion bonding in patent publications and other literatures, but they were little practical and none have been industrially applied.

3. Principles of Diffusion Bonding of Al-containing Stainless Steel Foils

The alumina film and surface roughness of the foils are the factors to hinder the diffusion bonding of Al-containing stainless steel foils. It is therefore necessary to remove the alumina film and eliminate voids (gaps) at the contact areas between the foils for obtaining good bonding strength[5].

The alumina film on the foil surface is broken by evaporating Al in the foil material through a vacuum heat treatment at a high temperature. The broken film coagulates into small granules and the diffusion bonding proceeds at the surface devoid of the film. The Al evaporation, however, has to be controlled within an appropriate range since it decreases the Al content of the foil material and this, in turn, deteriorates the oxidation resistance.

It is also necessary to eliminate the voids at the contact areas for realizing strong bonding. The diffusion of vacancies is one of the mechanisms for the voids to disappear. Crystal atom vacancies are
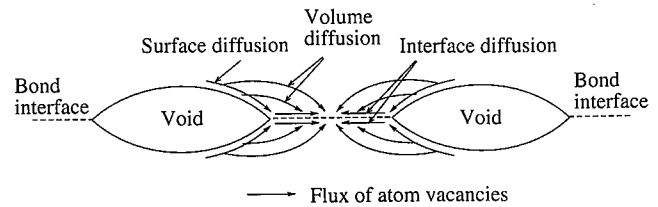

Fig. 1 Flux of atom vacancies contributing to void shrinkage in diffusion bonding

considered to diffuse through interface diffusion, surface diffusion and volume diffusion and the voids thus shrink, as illustrated in **Fig. 1**[8]. Generally speaking, the vacancies move more easily at the void surface and the bonding interface than in the bulk (inside crystals). It is the vacancies that helps atoms move, and the atoms move (diffuse) in the opposite direction to the vacancies coming to the bonding interface. The movements of the vacancies promote the diffusion, for the chemical potential of the vacancies is different at a void surface and at a bonding interface. The voids shrink and eventually disappear as a result of this phenomenon.

4. Optimization of Diffusion Bonding Parameters
4.1 Diffusion bonding parameters

Foil thickness, surface roughness, corrugation shape, temperature and time of the vacuum heat treatment and the degree of vacuum are among the principal parameters in the manufacture of the metal catalyst supports by the diffusion bonding method. These factors are intertwined with each other in so complex a manner in the real diffusion bonding process that their interrelations had not been clarified and, for this reason, conventional manufacturing technologies focused mainly on the heat treatment conditions. Through our researches, however, it became clear that foil surface properties and the corrugation shape had very significant influences over the diffusion bonding process besides the heat treatment conditions[6,7].

4.2 Influences of foil material and corrugation shape

Fig. 2 schematically illustrates contact portions of the flat foil and the corrugated foil. The stainless steel foils for the metal catalyst supports are produced by rolling and there are rolling marks in the rolling direction on the foil surfaces. **Fig. 3** shows an example of the foil surface roughness in the rolling direction (RaL) and in the direction in right angles to the rolling direction (Rac). The surface roughness in the direction in right angles to the rolling direction (width direction) is generally coarser than in the other direction.

Figs. 4 (a) and **(b)** are conceptual sectional views of a bond portion before and after the bonding as viewed along the arrow in Fig. 2.

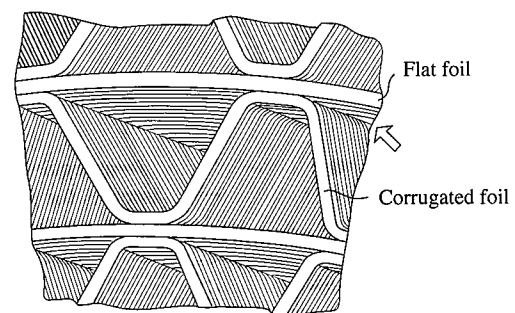
Fig. 2 Schematic illustration of contact portions of flat and corrugated foils
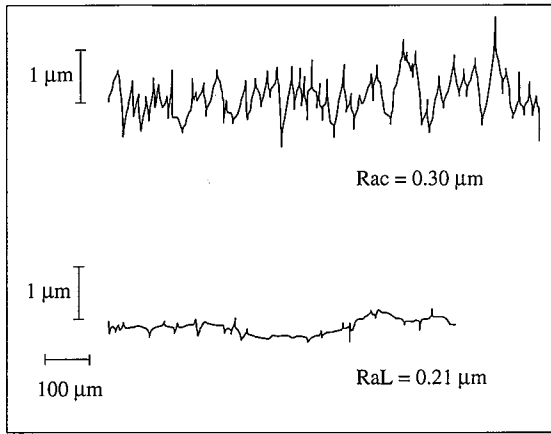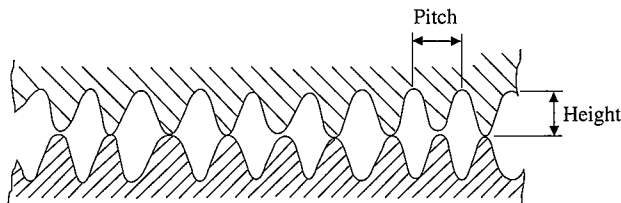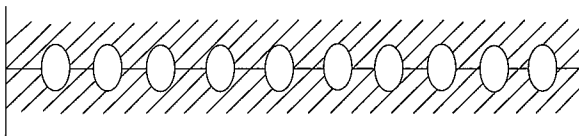
Fig. 3 Foil surface roughness

(a) Before diffusion bonding

(b) After diffusion bonding

Fig. 4 Conceptual sectional views of bond portion before and after diffusion bonding

Fig. 5 PPI and diffusion bonding performance

Fig. 6 Trapezoidal corrugation

There are voids after the bonding process as shown in Fig. 4 (b) and the bonding strength can be increased by decreasing the number and size of the voids, and control of the foil surface roughness, especially that along the foil width, is very significant for achieving this. The authors measured the number of surface peaks per 1 inch along the width denominating the number PPI, and examined the relation between the PPI and diffusion bonding performance of foils. As a result, it turned out that the larger the PPI the better became the diffusion bonding performance as shown in **Fig. 5**.

It was also confirmed that the thinner the foils the better the diffusion bonding performance because of more intimate contact between the flat and corrugated foils.

Following that, the influence of the corrugation shape was investigated. The flat and corrugated foils are known to be oxidized during the vacuum heat treatment by residual oxygen at the commonly used degree of vacuum of 10^{-4} Torr or so. It is suspected that, when the contact area is narrow, the oxygen penetrates between the contact surfaces to form Al_2O_3 adversely affecting the diffusion bonding process. For accelerating the diffusion bonding, therefore, it is better to make the contact area as broad as possible. It is ideal to corrugate the foil into a trapezoidal curve as shown in **Fig. 6**.

4.3 Clarification of optimum ranges of diffusion bonding parameters

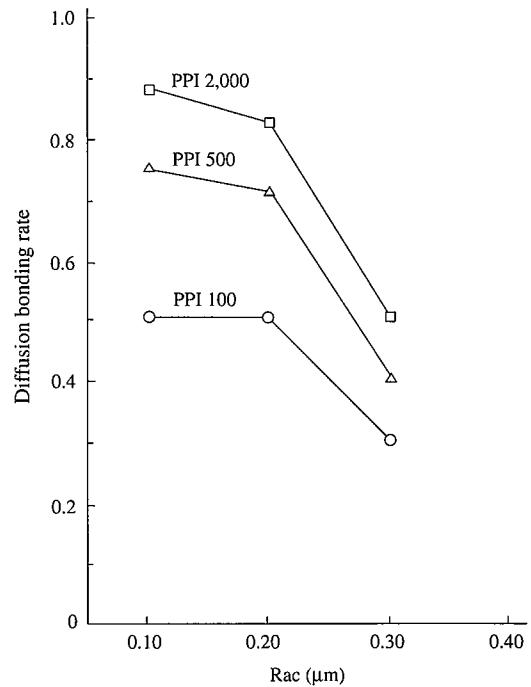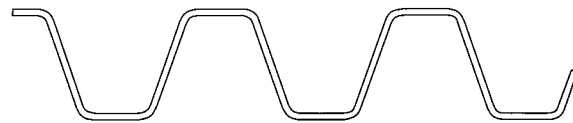In parallel to the examination of the foil materials and the corrugation shape described above, we evaluated the conditions of the vacuum heat treatment (temperature, time and degree of vacuum), in pursuit of a method to define manufacturing conditions of the diffusion bonding through overall consideration of all the principal factors influencing the bonding process. What was aimed for was, namely, a manufacturing method to secure the diffusion bonding strength by accelerating the Al evaporation and, at the same time, the oxidation resistance of the foils.

For the purpose of expressing the Al evaporation condition, a dimensionless number λb was newly introduced as follows:

$$\lambda b = \sqrt{\left\{ \left(2kT \times K_1 \times \sqrt{(1/T)} \right) / \left(\delta_z \times D_0 \times \exp\left(-Q_p / RT \right) \right) \right\}} \times b$$

$$\cdots(1)$$

Note that we clarified through tests that the following relation held true between the saturated vapor pressure of Al P_s and the degree of vacuum P_{out}:

$$P_s = K_2 \times \exp(-Q / RT) \quad 8 \quad \times P_{out} \qquad \cdots\cdots(2)$$

The constants in the above expressions are as follows:
$K_1 = 6.69 \times 10^{24}(s^{-1}Pa^{-1}m^{-2}K^{-1/2})$
$K_2 = 7.52 \times 10^9(Pa)$
$Q = 291.0(KJ \cdot mol^{-1})$
$Q_p = 250(KJ \cdot mol^{-1})$
$D_0 = 1.905 \times 10^{11}(m^2s^{-1})$
$R = 8.31(J \cdot K^{-1} \cdot mol^{-1})$
$k = 1.38 \times 10^{-23}(J \cdot K^{-1})$
δ_z: average gap between flat and corrugated foils
δ_z can be expressed as follows because it changes in proportion to

the geometrical moment of inertia and average surface roughness of the foils and in inverse proportion to the surface pressure:

$$\delta_z = f(\delta f^2, F/b, Ra) \qquad \cdots\cdots(3)$$

Our experiments made it clear that equation (3) could be approximated by the following equation:

$$\delta_z = C_1 \times \delta f^2 \times 1/(F/b) \times Ra \qquad \cdots\cdots(4)$$

where, C_1 is constant of proportion, δf is foil thickness (m), Ra is the average surface roughness of foils (m), F is the back tension at the foil coiling (kgf), and b is the width of the contact area between the flat and corrugated foils (m).

The following equation is obtained from the constants and equations (1) and (4):

$$\lambda b = C \times \delta f^{-1} \times F^{1/2} \times Ra^{-1/2} \times T^{1/4} \times \exp(15000/T) \times b^{1/2} \qquad \cdots\cdots(5)$$

$$\text{(C: constant of proportion} = 6.8 \times 10^{-12})$$

Also, the following expression is obtained from expression (2) by substituting the constants:

$$7.52 \times 10^9 \times \exp(-35000/T) \quad 8 \quad \times P_{out} \qquad \cdots\cdots(6)$$

As a result of experiments to determine the range of the value of λb where both the diffusion bonding strength and the oxidation resistance are satisfactorily realized, good figures were obtained in the range of 8 λb 20. Namely, we discovered that the diffusion bonding had to be conducted under the condition defined by expression (6) and 8 λb 20.

This result was applied to the manufacturing process of the metal catalyst supports and an optimum manufacturing condition was established.

5. Development of Bonding Structure of Diffusion-bonded Metal Catalyst Support

The manufacturing condition of the diffusion-bonded metal catalyst support was described in the preceding section. What came next as a point to be tackled was development of a bonding structure withstanding the rapid heating by the exhaust gas and cooling thereafter. The diffusion-bonded metal catalyst support is manufactured by coiling the flat and corrugated foils to form a honeycomb body and the honeycomb body undergoes the vacuum heat treatment inserted in an outer cylinder. If the vacuum heat treatment is done to the as coiled honeycomb body, it will be bonded in its entirety, forming too rigid a structure to be durable through violent thermal stress. When the metal catalyst support is rapidly heated, only its center portion becomes hot and expands mainly in the axial direction and, if the entire honeycomb is bonded, strain is created inside it owing to the restriction by the bonding, and is destroyed by repeating the process.

The measures to overcome this problem were study and a bonding structure excellent in structural durability was developed as shown in **Fig. 7**. In this structure, whereas the center portion of the honeycomb body is bonded by the diffusion bonding, non-bonded portions are created near the periphery to facilitate the axial expansion/contraction of the honeycomb body. An excellent structural durability was obtained through this structure.
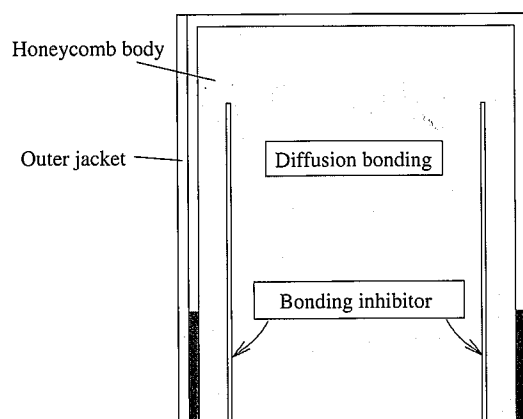

Fig. 7 Sectional view of bonding structure of diffusion-bonded metal catalyst support

6. Closing

Higher gas cleaning performance at lower costs is increasingly required of the catalyst supports, as the regulations on the car exhaust gas are becoming more and more stringent. For obtaining better gas cleaning performance, the recent trend is that the catalyst supports are mounted closer to the engines, which requires a high structural durability of the supports. Nippon Steel has commercially applied metal catalyst supports of 30-μm thick foils excellent in gas cleaning performance and, further, developed a metal catalyst support of ultra thin foils, 20 μm in thickness. Other technologies are being developed and proposed to enhance the gas cleaning performance yet more.

The diffusion-bonded metal catalyst support, which has been commercially applied, is manufactured by a method fundamentally different from conventional methods. It is free from the defects of the brazing-bonded supports and can be manufactured at a lower cost, maintaining an equally high durability. The diffusion bonding technology is expected to be applicable also to various other honeycomb products.

Nippon Steel will continue expanding the market through development of new high-cost-performance metal catalyst supports applying these new technologies.

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