1. Introduction

For application to the catalytic converter in an automotive exhaust gas purifier, Nippon Steel Corporation has developed and commercialized a metal substrate using a honeycomb body made of stainless steel foils as a substitute for a ceramic one. The metal honeycomb body is manufactured by spirally winding flat and waved stainless steel foils, approximately 50 μm thick, one over the other. Since a catalytic converter is exposed to high-temperature exhaust gas during operation, the joints between the foils of a metal honeycomb body must have a high bonding strength stably at high temperatures. However, because the foils must be bonded to each other after being wound into a honeycomb body and they are very thin, it is difficult to apply sufficient pressure to contact surfaces to secure a good bonding strength. In view of this, it is necessary to employ a joining method that offers strong bonding stably under a very low contact pressure; (1) brazing and (2) diffusion bonding satisfy such requirements. This article gives outlines of these joining methods and discusses their application to a metal substrate.

2. Brazing

2.1 Outline of brazing

Brazing is a joining method wherein a filler metal having a lower melting temperature than those of base metals is used, and thus the base metals are joined virtually without melting. Since the bonding is effected as a result of the wetting of base metals with molten filler metal, no pressurization is required at the surfaces to be joined, and for this reason, the method is suitable for bonding a honeycomb body made of thin foils. A variety of filler metals are available for different base metals and applications; in consideration of heat resistance and cost, Ni-base filler metals in powder manufactured by gas atomization are used for bonding the honeycomb body of a metal substrate.

2.2 Wettability

The wettability of base metals with molten filler metal is important for the bonding quality of brazing. The stainless steel foils used for the honeycomb body contain Al to improve resistance to oxidation. Fig. 1 shows the relationship between the Al content of the base metal and spreading ratio, which is the ratio between the projected areas of filler powder before and after melting, as schematically illustrated in the graph area; the larger the ratio, the better the wetting of the base metal with the filler metal. The filler powder used here was BNi-5 of a 19%Cr-10%Si-Ni. As the graph shows, the spreading ratio decreases as the Al content of the base metal increases; this is because aluminum oxide on the foil surface hinders wetting. The atmosphere at brazing work is important for securing good wettability. Fig. 2 shows the effect of brazing atmosphere on the spreading ratio; the base metals were a stainless steel foil of a 20%Cr-5%Al-Fe alloy and other comparative materials, the filler powder was BNi-5, and the atmospheres tested were a vacuum and hydrogen. As seen here, wettability is better in the reductive hydrogen atmosphere. However,
there is a problem with brazing in a hydrogen atmosphere: such an atmosphere may contain oxygen under poor dew-point control, and good atmosphere control is essential in industrial application. Brazing is possible also in a vacuum, but careful control of the degree of the vacuum is required.

2.3 Brazing temperature

Wetting results from reaction between a base metal and molten filler metal at their boundary surfaces, and for this reason, brazing temperature has significant effects on wettability. Fig. 3 shows the relationship between brazing temperature and spreading ratio; the base metals used here were stainless steel foils of a 20%Cr-5%Al-Fe alloy, the filler powder was BNi-5, and the atmosphere was a vacuum. As seen with the graph, spreading ratio fluctuates when the temperature is not sufficiently high. Therefore, to obtain a good bonding joint, it is necessary to heat the materials to sufficiently high temperatures.

2.4 Brazing of honeycomb body

Fig. 4 shows photographs of a metal honeycomb body at high magnifications; the flat and waved foils are bonded to each other by brazing. Adequate control of brazing conditions makes it possible to obtain a metal honeycomb body with sufficiently high bonding strength.

3. Diffusion Bonding

3.1 Diffusion bonding of honeycomb body

Diffusion bonding is a method for forming a bonded joint by applying pressure to the contact areas of base metals and heating them to cause diffusion of their component elements. However, with a honeycomb body of stainless steel foils, it is impossible to apply the pressure sufficient for diffusion bonding to the contact areas for the following reason: when winding a flat foil and a waved foil, the latter being made by corrugating a flat foil, into a honeycomb body, contact pressure is imposed by applying back tension to the flat foil, but if the back tension is too strong, the center portion of the honeycomb body buckles. Because of this impossibility of applying a sufficiently high back tension, the surface condition of the foils has a significant influence over the bonding quality in the diffusion bonding of a metal honeycomb body. The following sub-sections describe this aspect in more detail.

3.2 Joining conditions

Flat, heat-resistant, ferritic stainless steel foils of a 20%Cr-5%Al-Fe alloy 52 μm thick were used as specimens. A waved foil was prepared by corrugating a flat foil to a wave height of 1.25 mm and a wave head width of 0.5 mm at a pitch of 2.5 mm. The degree of vacuum of the vacuum furnace used was approximately 2 × 10⁻⁴ Torr, and the heating temperature was 1250 °C.

3.3 Effects of alumina formation

To study the effects of vacuum heating on the surface properties of a foil, a foil laid flat on the floor of the furnace was heated in a vacuum for 90 min. At the end of the heating, the color of the upper surface (face) of the foil turned into grayish white, while that of the lower surface (back) retained the original metallic luster. Fig. 5 shows SEM-EDS micrographs of the foil surfaces; whereas the face side was covered with white powder, the back side was substantially in black with scattered white portions. EDS analysis revealed that the
black portion was the Fe-Cr-Al base metal and the white portion was alumina. This indicates that residual oxygen in the furnace atmosphere oxidized the face side exposed to the vacuum furnace inside, and on the other hand, the oxidation was suppressed on the back side, which contacted the furnace floor. This is presumably because aluminum vapor emitted from the back side stayed between the foil and the furnace floor to prevent oxygen from oxidizing the surface.

The above indicates that successful diffusion bonding of a metal honeycomb body depends upon aluminum vapor emitted from the foils to stay near the contact portions of the foils to inhibit oxidation of the surfaces to be joined. For this to take place, corrugation in a trapezoidal curve is more advantageous than that in a sine curve. Note that once alumina forms on the contact surfaces, diffusion bonding is impossible.

3.4 Effects of surface roughness

The surfaces of flat and waved foils are covered with very small roll marks running in the rolling direction as Fig. 6 illustrates. Fig. 7 is an enlarged, schematic sectional view of a contact portion in the direction of the arrows in Fig. 6; as seen here, the two foils contact each other at the peaks of the roll marks. It is easy to reason that the roughness (pitch and height of roll marks) of the surfaces significantly influences the quality of diffusion bonding under the condition of a low contact pressure. Fig. 8 is a schematic sectional view of a joint between flat and corrugated foils by diffusion bonding. As seen here, there are many voids on the joint plane; for the description below, the total length of the bonded portions excluding the voids per unit sectional length is defined as diffusion bonding rate. The surface finish of the rolls was changed for the finish rolling of the foils from #80 to #400, as a result, the roughness in Ra of the foil surfaces decreased from 0.35 to 0.10 μm, and the diffusion bonding rate after bonding for 90 min improved from 0.25 to 0.50. At durability test using an automobile engine at an inlet gas temperature of 950 °C, while the metal substrate made of the foils rolled using the #80 rolls broke and fell after approximately 400 heat cycles, the one made of the foils rolled using the #400 rolls proved satisfactory, withstanding more than 900 heat cycles.

4. Closing

By optimally controlling the atmosphere and temperature of bonding work and the foil surface finish, it is possible to realize sufficiently high bonding strength of flat and waved foils even under the bonding condition of a very low contact pressure, and thus a honeycomb body of stainless steel foils for a converter substrate highly durable under high-temperature operating conditions can be manufactured. Fig. 9 shows such a metal substrate. The technologies and measures described hereinabove have led to the development of a metal converter substrate excellent in durability.