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Development of Ferritic Stainless Steel Foil as Metal Support for Automotive Catalytic Converter

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Abstract:

A metal support was developed for a catalytic converter to be installed right below the exhaust manifold of an automobile gasoline engine. The metal support must withstand the thermal fatigue and high-temperature oxidation of the punishing environment where it is exposed to an intermittent and high-velocity stream of hot exhaust gases from the engine. The overall design of its honeycomb foil and jacket material is as important as the joined structure of the metal support. The authors developed a new honeycomb foil steel for the automotive catalytic converter while paying due consideration to the service performance of the metal support; efficiency of stainless steel mass-production process via the basic oxygen furnace steelmaking-continuous casting route; and formability of the metal support. The basic composition of the metal support steel is a high-aluminum ferritic stainless steel containing rare earth metals, namely, low-carbon and low nitrogen 20Cr-5Al-0.05Ti-0.08Ln.

1. Introduction

The pollution of the global environment by automobile exhaust gases was pointed out earlier in the 1950s. In the United States, the low-emission vehicle (LEV) regulation was enacted first in California and then spread to other states. Japan enforced a similar law in 1975. In this process, three-way catalysts were developed to reduce automotive emissions of nitrogen oxides (NO_X), carbon monoxide (CO), and hydrocarbons (HC). A cordierite honeycomb (ceramic support) was developed to carry the three-way catalysts. Ceramic catalytic converters have been installed on about 1 billion automobiles to date.

The basic idea of using a metal honeycomb as the catalyst bed was proposed in the United States in 1960. In 1970, the Atomic Energy Authority of the United Kingdom applied for a patent on the idea of using Fe-Cr-Al as metal honeycomb material and applying a wash coat through the oxide film of Al_2O_3. In the 1980s, automobile parts manufacturers mainly in West Germany started the commercial use of stainless steel foil metal honeycombs for the purpose of improving the exhaust gas resistance, heat resistance, and light-off that are weaknesses of conventional ceramic honeycombs[1,2].

The above moves prompted first Nissan Motor[3] and then Toyota Motor to study metal honeycombs in Japan. Nippon Steel started joint research on metal honeycombs with Toyota Motor

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and Nippon Kinzoku in 1986, and constructed a metal honeycomb plant in Nagoya in April 1991. The plant has shipped out about 1 million metal honeycombs to date[4,5].

This report reviews the history of technology development from the laboratory study of the ferritic stainless steel YUS205-M1 (20Cr-5Al-Ti-Ln) for metal honeycomb foil to the determination of field manufacturing conditions for the steel. The technology thus established is also described.

2. Basic Composition Design

Table 1[6] lists the properties required of the metal honeycomb foil. The principal consideration are the service performance of metal honeycombs, employment of the stainless steel mass-production process, and fabricability of metal honeycombs. The basic composition design of the ferritic stainless steel YUS205-M1 is discussed from the standpoint of these properties required of metal honeycomb foil.

2.1 Chromium and aluminum

Stainless steel foil used to fabricate metal honeycombs is as thin as about 50 μm. Since it is exposed to high temperatures, it must possess extremely high oxidation resistance. Taking into consideration its relatively low thermal expansion, excellent oxidation resistance, low cost and the conventional production process it undergoes. Chromium-aluminum ferritic stainless steel is best suited as the foil material. The authors optimized the chromium and aluminum contents from the point of view of oxidation resistance and high-temperature fatigue strength.

Fig. 1[6] shows the effects of chromium and aluminum contents on the oxidation resistance of Cr-Al steel in engine exhaust gases. Aluminum has a marked effect on the improvement of oxidation resistance, while the effect of chromium in improving oxidation resistance levels off at nearly 20%.

Table 1 Properties required of stainless steel foil for metal honeycomb

Foil quality	Foil manufacturability	Honeycomb fabricability
(1) Oxidation resistance (2) Thermal fatigue resistance (3) High-temperature strength (4) Microstructural stability	(1) Mass producibility and feasibility of BOF steelmaking-continuous casting route (2) Hot-rolled strip toughness (3) Cold rollability and foil rollability (4) Quality stability (productivity and yield)	(1) Foil shape and thickness tolerances (2) Surface quality and roughness (3) Brazeability (4) Catalyst supportability (5) Honeycomb quality stability

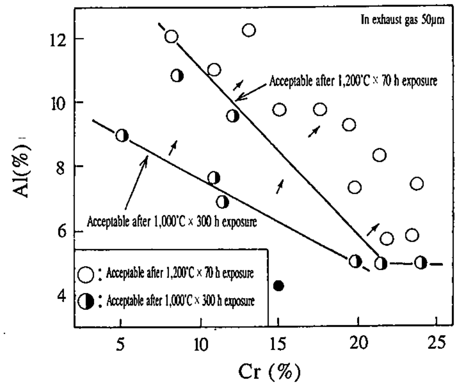

Fig. 1 Oxidation resistance map of lanthanoid-free Cr-Al steel

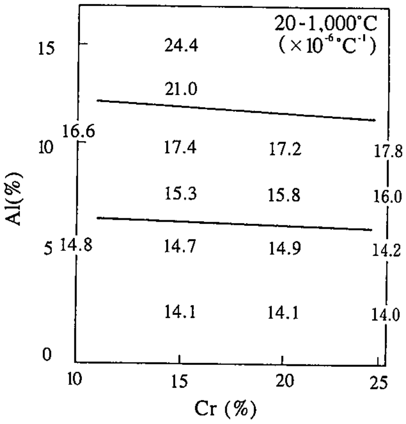

Fig. 2 Thermal expansion coefficient map of Cr-Al steel

Fig. 2[6] shows the average thermal expansion coefficient map of Cr-Al steel with respect to the chromium and aluminum contents. The thermal expansion coefficient does not appreciably depend on the chromium content, but increases with increasing aluminum content. Increasing the chromium content and decreasing the aluminum content are effective in maintaining good oxidation resistance and minimizing the thermal expansion that causes thermal fatigue. The effectiveness of chromium in improving oxidation resistance peaks at 20%, which means that the optimum chromium content is 20%. Taking this 20% chromium for granted, a Cr-Al steel with more than 5% aluminum is very low in cold workability and is difficult to mass produce. From what has been discussed above, the 20Cr-5Al steel is the best material for stainless steel foil for metal honeycombs.

2.2 Lanthanoids (lanthanum, cerium, and other rare-earth metals)

The oxidation resistance of stainless steel foil is generally inferior to that of a strip of the same composition. Very high oxidation resistance and especially good oxide film adhesion are required of stainless steel foil for metal honeycombs. This also serves the purpose of retaining the gamma-alumina layer (γ-Al_2O_3) (wash coat) as a direct catalyst carrier through the oxide film.

The addition of rare-earth metals (REM), such as titanium, zirconium and hafnium, is known to be effective in improving the adhesion of the oxide film to the Cr-Al steel. The optimum amount of the cost-effective lanthanoids to be added to the 20Cr-5Al steel foil was determined. (Lanthanoids are a generic term for REM other than yttrium and scandium, used as mixtures of lanthanum, cerium, praseodymium, neodymium and the like, and abbreviated to Ln.)

The type and content of REM to be added are often judged from the oxidation life of foil. In the actual environment, however, the foil oxidation does not run to its limit, and the oxidation rate or oxidation rate constant K_P means in this case. **Fig. 3**[6,7] shows the effect of lanthanoid addition in improving the oxidation rate constant K_P of the 20Cr-5Al steel in air at 1,200°C. The optimum lanthanoid content is put at 0.08 wt%.

2.3 Titanium

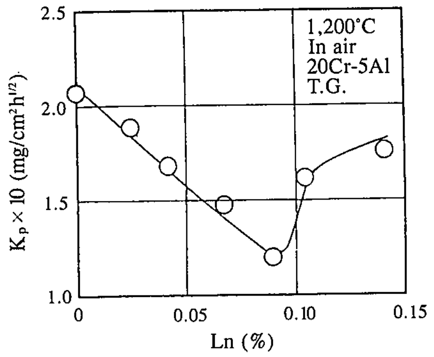

Fig. 3 Effect of lanthanoid content on oxidation rate constant K_P of 20Cr-5Al steel

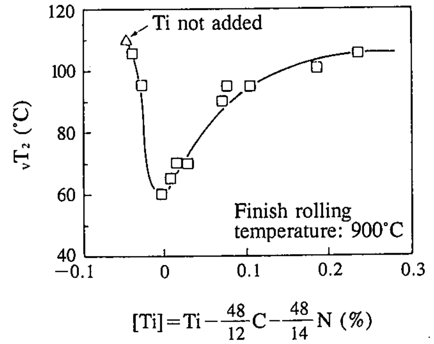

Fig. 4 Effect of titanium content on toughness of hot-rolled strip

High-chromium and high-aluminum steel like the 20Cr-5Al steel foil tends to crack in its production process, especially on the hot strip mill, which renders its mass production difficult. Adding titanium or niobium is effective against this problem. Titanium is selected here as alloying element. This is because the oxide film formed on the foil of niobium-containing steel tends to react with the wash coat, grow in thickness, and increase the creep elongation of the foil[6]. **Fig. 4** shows the effect of titanium in improving the toughness of hot-rolled strip as evaluated by the fracture appearance transition temperature $_vT_2$ in °C at which the Charpy impact value becomes 2 kgf · m/cm^2.

The optimum titanium content is determined in relation to the carbon and nitrogen contents. The toughness of hot-rolled strip is best improved when the effective aluminum content, that is, the amount of titanium to be added minus the amount of titanium to stoichiometrically combine with carbon and nitrogen, is zero; for example, titanium is added in the amount of 0.05% when the carbon and nitrogen contents are low. This amount of titanium is added to minimize the amount of precipitates that provide sites of brittle fracture initiation. The addition of titanium inhibits the grain-boundary precipitation of chromium carbides. When added to an excessive degree, however, titanium forms coarse titanium nitride (TiN), which serves as a site of brittle fracture initiation and lowers the toughness of the 20Cr-5Al steel.

Table 2 Basic composition of honeycomb foil steel

(wt%)

Cr	Al	Ti	Ln	C+N
20.0	5.0	0.05	0.08	≦0.0200

From the above results, the authors designed the basic composition of stainless steel foil for metal honeycombs as shown in **Table 2**.

3. Continuous Casting

Lanthanoid additions were made by way of wire insertion into the mold steel during the continuous casting of 20Cr-5Al steel. **Fig. 5**[8] shows the way the aluminum and lanthanoids in the molten steel transform the mold powder and change its melting temperature. Enriched with aluminum and lanthanoid oxides, the mold powder steeply rises in melting temperature. A new mold powder was designed for continuously casting the 20Cr-5Al steel. To the conventional powder developed for continuously casting high-aluminum stainless steel, low-melting point oxides were added in order to suppress the rise of melting temperature. Further, the silica (SiO_2) content was reduced to suppress the rise of viscosity due to the reduction of SiO_2 by aluminum and lanthanoids in the molten steel. The sodium oxide (Na_2O) content was also lowered to decrease the emission of white fumes of sodium carbonate (Na_2CO_3) and sodium fluoride (NaF) in the mold.

The segregation of lanthanoids in the surface layer of a continuously cast slab results in surface defects in the hot rolled strip, which is badly detrimental to the strip quality. The optimum lanthanoid wire melting position in the mold steel was studied to ensure the uniform lanthanoid distribution in the cast slab. **Fig. 6**[9,10] shows the segregation of lanthanoids in a slab of honeycomb foil steel when lanthanoid additions were not properly made. **Fig. 7**[9,10] shows the flow of the molten steel in the mold and the segregation of lanthanoids in the thickness direction of a slab as determined by fluid dynamic calculation. As can be seen

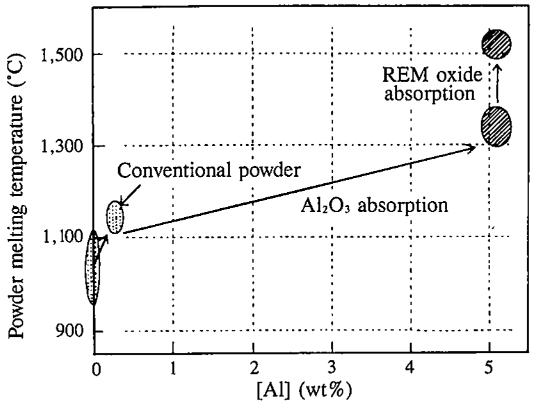

Fig. 5 Effect of steel aluminum content on melting temperature of mold powder

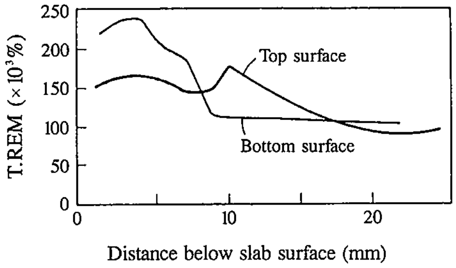

Fig. 6 Distributions of lanthanoids in thickness direction of slab

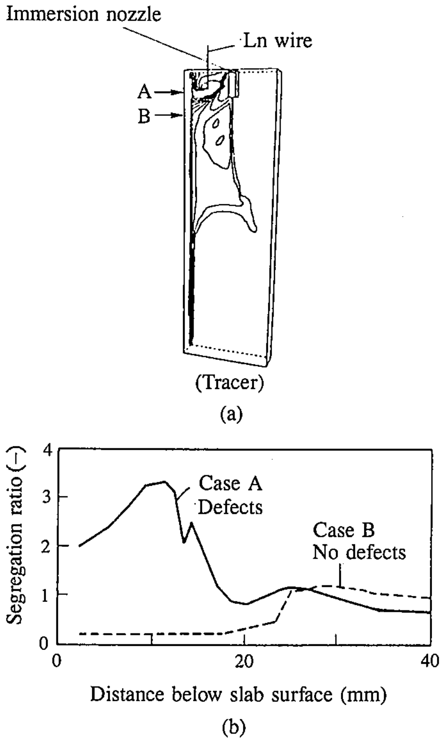

Fig. 7 Tracer distributions in continuous caster mold (a) and effect of lanthanoid wire melting position on lanthanoid segregation (b)

from **Fig. 6**, the lanthanoid segregation is considered to occur when the lanthanoid wire is melted near the meniscus and not at the midthickness of the mold (position A in **Fig. 7**). In other words, the lanthanoid segregation can be prevented if the lanthanoid wire is controlled to melt near the bottom of the immersion nozzle discharge stream and at the midthickness of the mold (position B in **Fig. 7**). A method of securing uniform lanthanoid distribution in the cast slab was established by optimizing the structure and feeding method of the lanthanoid wire on the basis of the above-mentioned findings and actual continuous casting operations. The new lanthanoid wire adding method proved effective in preventing the segregation of lanthanoids in continuously cast slabs.

4. Hot Rolling

The toughness of hot-rolled strip is influenced by its microstructure as well as by precipitates as discussed previously. Hot rolling conditions, particularly finish rolling temperature and coiling temperature, are important in this respect. **Fig. 8**[11] shows the effect of finish rolling temperature on the toughness of hot-rolled strip as evaluated by the fracture appearance transition temperature ${}_vT_2$. The optimum finish rolling temperature is 890°C. Raising the finish rolling temperature from that level coarsens the grain size, while lowering it allows high-density dislocations to remain to increase internal strains, both to the detriment of steel toughness. **Fig. 9**[11] shows the effect of coiling temperature on the toughness of hot-rolled strip. As indicated, the toughness of hot-rolled strip can be improved by lowering the coiling temperature. The coiling temperature is closely related to the precipitation of carbonitrides. The lower the coiling temperature, the smaller the segregation of chromium carbides.

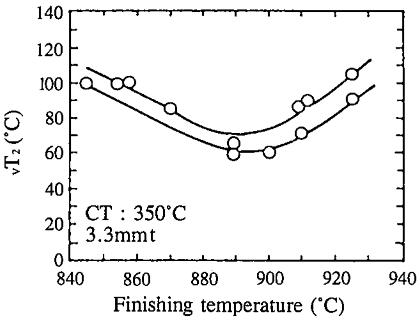

Fig. 8 Effect of finishing temperature on toughness of hot-rolled strip

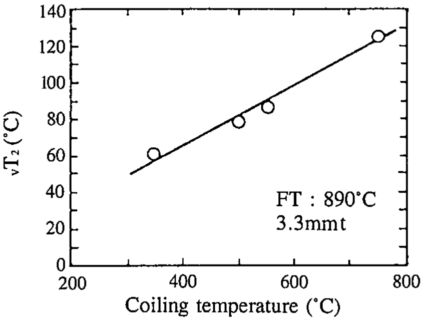

Fig. 9 Effect of coiling temperature on toughness of hot-rolled strip

5. Cold Rolling and Foil Rolling

The 20Cr-5Al-Ti-Ln steel is microstructurally made up of ferrite alone, is not transformed from the high temperature of continuous casting to the low temperature of cold rolling, and need not be handled with special care in metallurgical terms during cold rolling and foil rolling. When the new steel is to be made by the conventional mass-production process, that is, the BOF steelmaking-continuous casting-hot rolling-cold rolling-foil rolling route presented in this report, production yield and efficiency are very important factors.

Though not described in detail here, optimum metal honeycomb foil manufacturing conditions were established by feeding back such conditions as intermediate heat treatment during cold rolling, reduction distribution during foil rolling, and foil shape during finishing, respectively to the process steps concerned. The final step of foil fabrication into metal honeycombs was also taken as part of Nippon Steel's technology, and the plastic working conditions of foil at the metal honeycomb manufacturer were investigated in detail. An integrated metal support foil manufacturing process was thus established.

Similar improvements were incorporated in other facets of technology to ensure foil brazeability and catalyst supportability.

6. Brazeability

Corrugated and flat foils were vacuum brazed to form a metal honeycomb by using the nickel-base heat-resistant filler metal BNi-5 (JIS Z 3265, 19Cr-10Si-Ni bal.).

Brazing joins workpieces at faying surfaces by making use of the wettability of filler metal, and produces strong joints. It is best suited for joining honeycomb foils. Typical honeycomb foil brazed joints are shown in **Photo 1** and 2[12].

The metal honeycomb foil steel contains about 5% aluminum

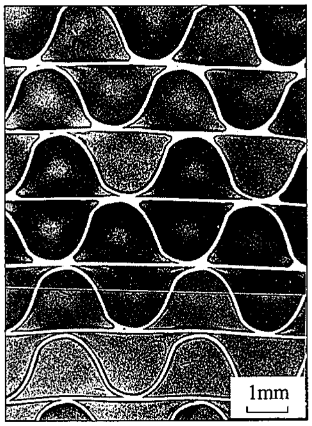

Photo 1 Macroscopic appearance of honeycomb

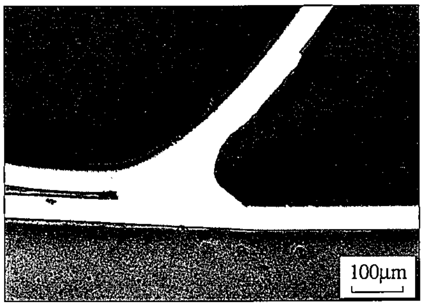

Photo 2 Macroscopic appearance of braze in honeycomb

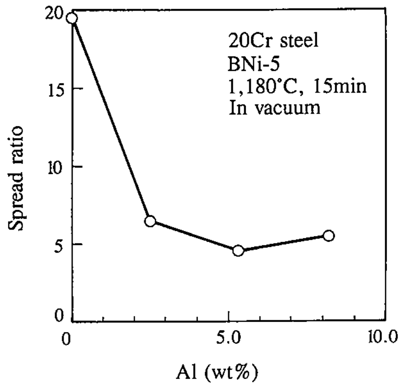

Fig. 10 Effect of aluminum content on spread ratio

for oxidation resistance. The aluminum has a great effect on the wettability of the brazing filler metal. **Fig. 10**[12] shows the effect of aluminum on the wettability of the filler metal. The wettability of the filler metal was evaluated by the ratio of the filler metal projected area on the base metal before brazing to that after brazing, as shown in **Fig. 11**[13]. As shown in **Fig. 10**, when the base metal contains 2.5% aluminum, the spreadability of the filler metal is reduced to about a quarter of that recorded when the base metal contains no aluminum. This is probably because the oxidation of aluminum in the base metal during brazing heat treatment forms such a film on the base metal surface as to reduce the spreadability of the filler metal on the base metal[12]. A high-vacuum brazing atmosphere is required to obtain good brazes.

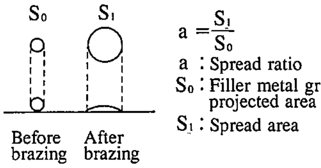

Fig. 11 Measurement of spread ratio

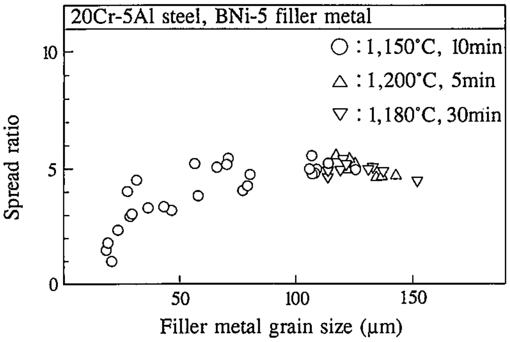

Fig. 12 Effect of filler metal grain size on spread ratio

Fig. 12 shows the effect of filler metal grain size on filler metal spreadability. The spread ratio is practically constant when the filler metal grain size is 60 μm or more and decreases as the grain size falls below 60 μm. Decreasing the filler metal grain size is considered to increase the ratio of the surface area to the volume of the filler metal and to accentuate the effects of the surface tension and surface oxides[13]. In this way, it is important to braze metal honeycomb foils by carefully controlling the composition and grain size of the brazing filler metal, the brazing atmosphere, and other relevant conditions.

7. Summary

1) The basic composition of stainless steel for metal honeycomb foils for automotive catalytic converters was set at 20Cr-5Al-Ti-Ln with low carbon and nitrogen contents.
2) The basic composition 20Cr-5Al was judged optimum in view of the oxidation resistance and thermal fatigue resisitance of the foil steel.
3) The lanthanoid content was set at 0.08% to improve the oxidation resistance of the foil steel and especially the adhesion of the Al_2O_3 film.
4) The titanium content was set at 0.05% to enhance the toughness of hot-rolled strip. The carbon and nitrogen contents were also controlled from the point of view of ensuring the strip toughness.
5) Adoption of the BOF steelmaking-continuous casting route was made feasible by designing a mold powder that is not transformed by aluminum or lanthanoids, and by making uniform lanthanoid distribution in the mold steel. The lanthanoid wire was controlled to melt near the bottom of the immersion nozzle discharge stream and at the midthickness of the mold.
6) Hot rolling conditions were established from the standpoint of strip toughness. The optimum final finish rolling temperature at the hot strip mill is 890°C. A low coiling temperature is favorable.
7) Cold strip rolling and foil rolling conditions must be deteminned from the point of view of foil fabrication into honecomb cores, catalyst support characteristics, and other factors involved.

8) A nickel-based heat-resistant filler metal was adopted for brazing the honeycomb foils. Selecting the pressure of vacuum heat treatment and other brazing conditions is important in making good foil brazes in the honeycomb.

8. Conclusions

The process from the development to the commercialization of metal honeycomb foil steel may be divided into two phases: research and development of basic technologies and buildup of applied manufacturing techniques and know-how. Alloy design of the foil steel, metallurgy concerning hot rolling conditions, foil manufacture, and fabricability of foils to honeycombs belong to the former phase. BOF steelmaking, and foil surface quality adjustment are among the factors belonging to the latter phase. Manufacture of the metal honeycomb foil steel via the BOF steelmaking-continuous casting route involved the development of purely basic technologies, however. Very high hurdles had to be surmounted in this course.

Production of the ferritic stainless steel YUS205-M1 (20Cr-5Al-Ti-Ln) by the world's first commercial BOF steelmaking-continuous casting combination is smoothly growing with warm user acceptance for high product quality. The properties required of automotive catalytic converter materials are expected to increase in severity, with intensifying environmental regulations on a worldwide level. Under these circumstances, new catalytic converter materials will continue to be developed at a faster pace, always with a view to high cost performance and changing user needs relative to the global environmental problem.

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