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Present and Future Trends of Materials for Automotive Exhaust System

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Abstract:

Stainless steel came to be used in automobiles to meet the social needs for clean exhaust gases and reduced weight for better fuel economy. The consumption of stainless steel for automotive use has almost quadrupled in the past decade. Stainless steel is used for the most part as material for the exhaust system. Type 409 was the original choice, but various other types of high-performance stainless steels are now used in the automobile exhaust system. This paper describes the past changes and future prospect of materials used for specific automotive exhaust system parts, namely, the gasket, manifold, front pipe, flexible pipe, metal catalyst carrier, and muffler.

1. Introduction

The United States pioneered the application of type 409 stainless steel to the exhaust system of automobiles in the 1960s. Japan begun to use type 409 and other stainless steels in the 1970s when automobiles came to be equipped with three-way catalytic converters to meet intensifying regulations over exhaust gas emissions. In 1989, Japanese automakers extended the service life warranty period of exhaust system parts to 3 years or 60,000 km, whichever comes first. This extension of warranty period accelerated the switchover from hot-dip aluminized carbon steel to stainless steel in this application. Today, stainless steel is used in almost all exhaust system parts from the cylinder head gasket to the tail pipe as shown in **Fig. 1**[1,2].

The consumption of stainless steel in the exhaust system per passenger car varies from model to model but averages about 15 kg per car as estimated from the weight by part column of **Table 1** and available statistics of the stainless steel usage (about 20% for the exhaust manifold and nearly 100% for the front pipe and other exhaust system parts downstream). Since Japan's passenger car production is about 9.38 million units per year (1992 data), stainless steel consumption in the exhaust system area is put at about 140,000 tons per year. This figure indicates a steel increase in recent years in the scale of the stainless steel market[3,4].

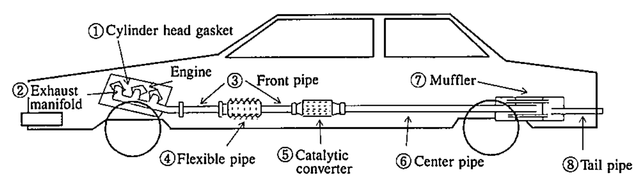

Fig. 1 Component parts of exhaust system of automobile

The substitution of stainless steel for hot-dip aluminized carbon steel in the exhaust system of passenger cars that account for about 75% of the total automobile production is nearly 100%, except for the exhaust manifold. In the future, however, the stainless steel consumption in this field of application is not expected to grow as rapidly as in the past. Instead, it is expected to slowly increase in the exhaust system of diesel-powered automobiles, mainly trucks, to meet the growing social demand for stricter exhaust gas emission regulations.

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Table 1 Service temperature and steel grade by type of exhaust system part

No.	Part	Service temperature(°C)	Steel grade	Weight (kg/unit)
①	Cylinder head gasket	100	SUS301L	0.3
②	Exhaust manifold	950-800	YUS409D, YUS180	4
③	Front pipe	800-600	YUS409D,YUS436S, YUS180	2
④	Flexible pipe		SUS304, SUSXM15J1, SUS302B	0.5
⑤	Catalytic converter		YUS205M1	2
⑥	Center pipe	600-300	YUS409D, YUS436S, YUS432	3
⑦	Muffler	300-100	YUS409D, YUS436S, YUS432, NSA1YUS409D, NSA1YUSA32	6
⑧	Tail pipe		YUS436S, YUS432, NSA1YUS409D	

YUS409D: 11Cr-0.2Ti, YUS436S: 17Cr-1.2Mo-0.2Ti, YUS432:17Cr-0.5Mo-0.2Ti, SUS301L: 17Cr-7Ni,
YUS205M1: 20Cr-5Al-Ln, YUS180: 19Cr-0.4Nb-0.4Cu-0.4Ni, SUSXM15J1: 18Cr-13Ni-4Si.
NSA1YUS409D and NSA1YUS432 are hot-dip aluminized stainless steels.

As in the United States, type 409 was initially the only type of stainless steel used in automobile exhaust systems in Japan. Recent years have seen mounting needs for the development of high-performance stainless steels, including ferritic stainless steel with high heat resistance for exhaust manifolds for improved fuel economy; austenitic stainless steel with high elevated-temperature salt corrosion resistance for flexible pipes for better noise control; and ferritic stainless steel with high corrosion resistance for mufflers for longer corrosion performance. The stainless steels listed in **Table 1** are answers to these needs. The recent business recession in Japan has increased the demand for the development of new stainless steels in order to reduce cost without sacrificing quality.

In the United States and Europe, type 409 is a standard exhaust system material, and high-chromium ferritic stainless steel is used where higher functionality is required. In Europe, austenitic stainless steel is also used along with ferritic stainless steel[5].

2. Present State and Future Outlook of Exhaust System Materials

2.1 Cylinder head gaskets

Cylinder head gaskets were formerly made of asbestos, but the fear of the toxic effect of asbestos on the health of people stiffened government regulations over the industrial use of asbestos. This problem, coupled with the gas seal tightness problem following the increase of engine output, prompted the replacement of asbestos with other gasket materials. Today's gasoline engine cylinder head gaskets are made mostly of graphite. Metal gaskets are used mainly on diesel engines.

Metal gaskets are made by beading and laminating three to four sheets of high-strength stainless steel. SUS301L is a principal type of stainless steel used to make metal gaskets. Metal gaskets are advantageous over asbestos gaskets in terms of heat resistance, thermal conductivity, sag resistance, maintainability, and pollution control.

Nippon Steel developed the SUS301L shown in **Table 1** as material for single-layer gaskets for passenger car engines. SUS301L can be made available in a wide range of mechanical strength by cold working, has the carbon content reduced to improve the intergranular corrosion performance of welds, and features excellent workability and toughness after cold rolling. The single-layer metal gasket can assure sufficient seal tightness between the cylinder head and the cylinder block by the excellent spring characteristics of stainless steel, thereby minimizing the strain of the cylinder bore.

Metal gaskets must have high strength and superior bead formability. The present single-layer gasket has a shim ring laser welded. A truly single-layer configuration is a future target. The development of gasket materials with high strength and ductility as well as excellent service performance is hoped for.

2.2 Exhaust manifold

The exhaust manifold is attached through flanges to the engine and exposed to hot exhaust gases. It has been traditionally made of cast iron like FCD41. In Japan, YUS409D and YUS180 ferritic stainless steels (2.0 mm thickness) that allow section thickness reduction and have excellent oxidation resistance and thermal fatigue resistance began to be used as exhaust manifold materials in the mid-1980s with the aim of reducing weight and increasing output. The proportion of cast iron is declining with increasing use of stainless steel, but 2.5-mm wall thickness exhaust manifolds can now be fabricated from stainless cast steel as a result of the development of the vacuum casting process. This type of exhaust manifold is used on some passenger car models where high elevated-temperature strength is particularly required[6,7].

Among the properties required of the exhaust manifold are oxidation resistance and thermal fatigue strength high enough to withstand hot exhaust gases; low thermal capacity to enhance the catalytic function; and good workability and weldability to increase the ease of installation in the automobile. The exhaust gas temperature will rise further in response to the Clean Air Act of the United States (exhaust gas emission regulation) to be enforced in the mid-1990s and to the improvement of high-speed fuel economy in Europe and other regions (see **Figs. 2** to **4**). Stainless steels with higher heat resistance are thus in demand. Another recent development is ferritic stainless steel that is improved in thermal fatigue properties by making use of solid-solution strengthening with niobium or molybdenum and is enhanced in oxidation resistance and microstructural stability in the service environment[8,9].

In the United States and Europe, attempts were made to use stainless steel in exhaust manifolds early in the 1980s. Ferritic stainless steels with a low coefficient of thermal expansion, such as types 409 and 439, are used mainly in the United States. In Europe, exhaust manifolds are made of nickel-base alloys or austenitic stainless steels to meet the high exhaust gas temperature of about 1,000°C resulting from high-speed running. Exhaust manifolds are also structurally designed to relax thermal strain[10].

To expedite the substitution of stainless steel, stainless steel exhaust manifolds, which are costlier than present cast iron exhaust manifolds, must be reduced in manufacturing cost. This means that stainless steel exhaust manifolds must be reduced in total cost, that is to say, in both material cost and fabrication cost.

Fig. 2 shows the effects of air fuel ratio on fuel economy and exhaust gas temperature. The effect of air-fuel ratio on exhaust gas composition at the engine outlet is shown in **Fig. 3**, while that on three-way catalytic converter performance is shown in **Fig. 4**. The effect of alloying elements on the 0.2% offset yield strength at 950°C of 19%Cr stainless steel is shown in **Fig. 5**[11,12].

2.3 Front pipe

The front pipe is located between the exhaust manifold and the flexible pipe. To enhance the catalytic action or exhaust gas cleaning action of the catalytic converter, the front pipe must minimize the heat lost by radiation and prevent the exhaust gas temperature from dropping. In the past, the front pipe was mostly a monolithic pipe. In recent years, thin-walled hollow double pipe (laser or TIG welded) has been actively developed in Japan and the United States to prevent the above-mentioned drop of exhaust gas temperature and to control noise.

Like the exhaust manifold, the front pipe is fabricated from YUS409D, YUS436S or YUS180 in Japan considering the exhaust gas temperature, in particular. YUS436S and YUS180 with superior oxidation resistance and corrosion resistance as well as their lower-cost versions will be increasingly used in the future in keeping with the rise of exhaust gas temperature and reduction of wall thickness.

As in Japan, type 409 is a standard front pipe material in the United States. In some cases, TIG-welded pipe of austenitic stainless steel is used as the inner pipe of the thin-walled hollow double pipe from the standpoint of workability. In Europe, type 321 austenitic stainless steel is still used as the front pipe material because of the high fabricability of electric resistance welded (ERW) pipes, but there exist strong needs for YUS180 and other ferritic stainless steels with low cost and low coefficient of thermal expansion.

Various types of thin-walled hollow double pipe are fabricated from ferritic to austenitic stainless steels for individual reasons in Japan, the United States, and Europe. In the future, the front pipe will be predominantly made of ferritic stainless steel that features excellent service performance properties such as oxidation resistance and thermal fatigue resistance, and is cost effective.

2.4 Flexible pipe

The flexible pipe is usually installed between the exhaust manifold and the catalytic converter to prevent the transmission of engine vibration to the exhaust system. It consists of bellows-shaped double pipe (0.3 to 0.4 mm in wall thickness) and covering stainless steel wire mesh (braider).

The flexible pipe is made from easy-to-work austenitic stainless steel considering weldability and severe hydrostatic bulge forming during fabrication.

As the flexible pipe is subject to high-temperature fatigue in the service environment, it is generally made from SUS304 in Japan. In frigid regions where deicing salt is used on roadways to prevent freezing in winter, the flexible pipe is exposed to a very severe environment combining high-temperature salt corro-

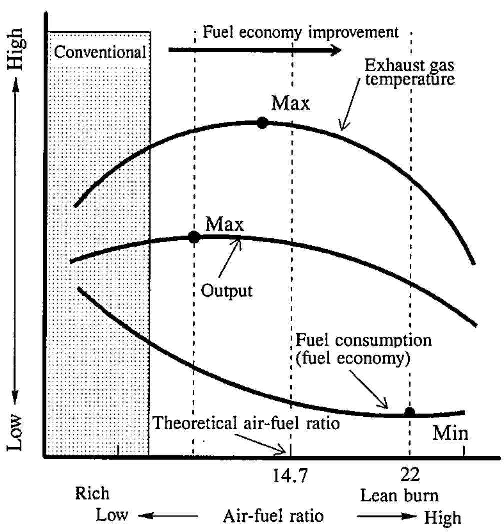


Fig. 2 Effects of air-fuel ratio on fuel economy and exhaust gas temperature

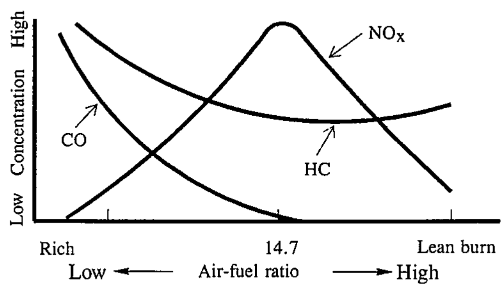


Fig. 3 Effect of air-fuel ratio on exhaust gas composition

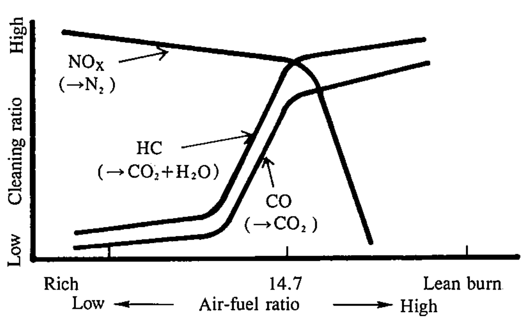


Fig. 4 Effect of air-fuel ratio on performance of three-way catalytic converter

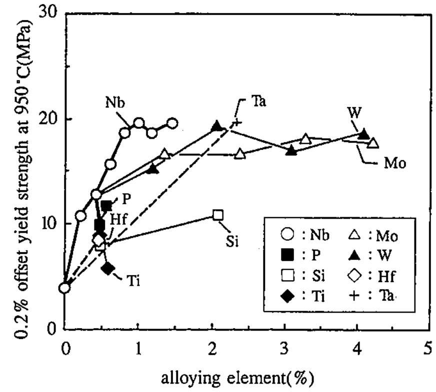


Fig. 5 Effect of alloying elements on 0.2% offset yield strength of 19Cr stainless steel at 950°C

sion with high-temperature fatigue. SUSXM15J1 with silicon addition and increased nickel content, and its modified version with a molybdenum addition and optimized chromium content are used to make the flexible pipe of automobiles intended for such frigid regions[13,14].

Flexible pipe of the interlocked multi-layer structure is adopted on car models to be used in a severe service environment. Several structural measures are taken to augment the material strength.

In North America and other regions suffering from severe deicing salt damage, stainless steel comparable to SUSXM15J1 exhibited perforation in a relatively short period of time. Given the perforation corrosion warranty for 10 years or 100,000 miles, whichever comes first, in North America, the flexible pipe will have to be improved in both material and structure.

2.5 Metal catalytic converter

The catalytic converter is mounted just below the exhaust manifold for cleaning the exhaust gas. Since it is used at elevated temperatures, an improvement in the durability of the catalyst carrier is an important issue. While the cordierite monolith is traditionally used as catalyst carrier, ferritic stainless steel foil with excellent thermal shock resistance and low heat capacity has come to be used in its place in recent years. The metal carrier is invariably exposed to rapid heating when the engine is started and accelerated as well as to localized thermal stress arising from radial temperature distribution. The stainless steel foil must be assembled into a honeycomb structure with excellent thermal fatigue resistance. **Photo 1** shows a general view of the metal honeycomb, and **Fig. 6** the metal catalytic converter.

The metal honeycomb core is composed of flat foil and corrugated foil (about 50 μm in thickness) of high-heat resistance ferritic stainless steel, which are spirally wound and brazed into a structure capable of withstanding high-temperature heat cycles[15].

The basic chemistry design of the foil material is discussed here. Chromium-aluminum ferritic stainless steel is a suitable foil material that can be produced by a conventional stainless steel production process, and it features relatively low thermal expansion and excellent high-temperature oxidation resistance. The coefficient of thermal expansion of the iron-chromium-aluminum alloy does not appreciably depend on the chromium content but increases with the aluminum content. The resistance of the alloy to oxidation in the engine exhaust gas levels off at the chromium content of 20%, as shown in **Fig. 7**[16]. The optimum chromium content is thus 20%, and the aluminum content should be low. Given the oxidation resistance of brazed joints, 20Cr-5Al is the optimum composition.

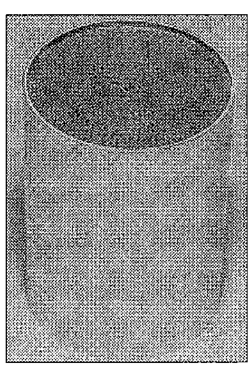


Photo 1 General view of metal honeycomb

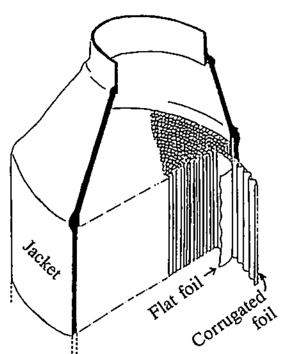


Fig. 6 Metal catalytic converter

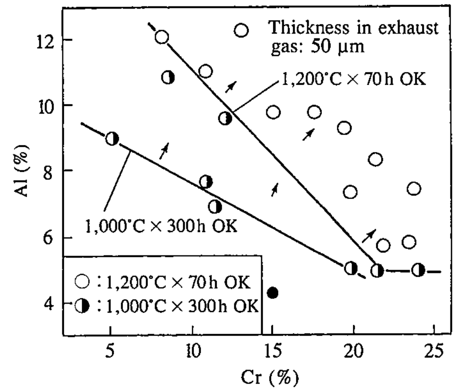


Fig. 7 Effect of aluminum and chromium contents on oxidation resistance of iron-chromium-aluminum alloy steel

Small additions of rare earth elements, such as hafnium, scandium, yttrium and cerium, are known to be effective in improving the oxidation resistance of iron-chromium-aluminum alloys, and the adhesion of oxide films in particular. **Fig. 8**[16] shows the improvement in the oxidation resistance of the 20Cr-5Al alloy achieved when rare earth elements other than yttrium and scandium, that is, lanthanoids (abbreviated as Ln), are added to the 20Cr-5Al alloy. The addition of Ln restricts the growth direction of the Al_2O_3 film to the inward diffusion of oxygen, inhibits the formation of voids at the Al_2O_3 film-base metal interface, and improves the adhesion of the Al_2O_3 film. Since an excessive addition of over 0.1% accelerates the oxidation of the 20Cr-5Al alloy, the Ln addition must be held within an optimum range.

A high-chromium and high-aluminum alloy such as the 20Cr-5Al alloy is susceptible to cracking on the production line and must be improved in hot-rolled sheet toughness. The situation can be effectively improved by reducing the carbon and nitrogen contents and adding titanium in an optimum amount. **Fig. 9** shows the relationship between the effective titanium content ([Ti] = Ti−48×[C]/12−48×[N]/14) and the Charpy impact value $_vT_2$ or temperature at which the Charpy impact value becomes 2 kgf · m/cm². The best toughness is obtained when [Ti] = 0. When no titanium is added, chromium carbide precipitates at grain boundaries and reduces the toughness of the 20Cr-5Al alloy. The grain-boundary precipitation of chromium carbide is suppressed by the addition of titanium. When titanium is added in an excessive amount, coarse-grained TiN serves as fracture

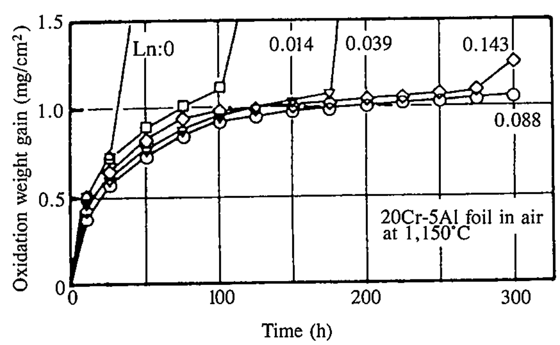


Fig. 8 Effect of rare-earth element additions (Ln) on oxidation resistance of Fe-20Cr-5Al alloy steel

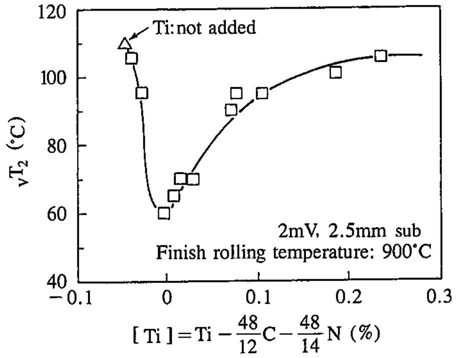


Fig. 9 Effect of titanium addition on improvement in hot-rolled sheet toughness of Fe-20Cr-5Al alloy steel

origin and again reduces the toughness of the 20Cr-5Al alloy[16,17]. These findings were utilized to determine the 20Cr-5Al-0.05Ti-0.08Ln-low C-low N composition (YUS205M1) as metal carrier foil material, and thus to manufacture the alloy on a conventional stainless steel mass-production line.

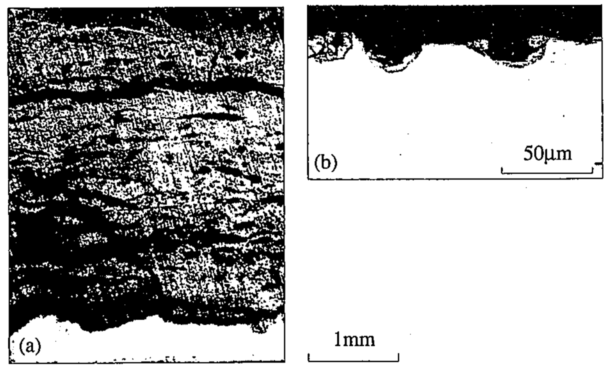
Metal carriers have many advantages, including low back pressure and excellent high-temperature durability. Because of their high cost, however, they are used in only about 4% of the catalytic converters in the world. The metal carrier is claimed to be effective in improving the exhaust gas cleaning performance of catalytic converters (in compliance with the LEV regulation of California in the United States) and is expected to increase in consumption. The 20Cr-5Al-REM composition will be applied to meet rising exhaust gas temperatures of up to 950°C. There is the possibility that low-cost and low-grade heat-resistant steels come to be used in such thermally moderate positions as under the automobile floor.

2.6 Muffler

In October 1989, automakers launched an exhaust system part warranty system from the standpoint of improved automobile safety, durability and, in particular, quality assurance. Mufflers are now guaranteed as general parts for 3 years or 60,000 km, whichever comes first. There are the following characteristic changes involving the muffler material. In 1978, the installation of three-way catalytic converters was mandated to prevent atmospheric pollution by exhaust gases, resulting in the formation of exhaust gas condensate in the muffler. In 1989, a system was established whereby mufflers are warranted for a service life of 3 years or 60,000 km, whichever comes first. The materials of mufflers have greatly changed to meet the needs of the times and changes in the social conditions.

Photo 2(a) and 2(b) respectively show the internal corrosion of an aluminized carbon steel muffler and a SUS410 stainless steel muffler each used for more than 2.5 years[18]. It is shown that general corrosion proceeded with the formation of a thick rust layer for the aluminized carbon steel muffler, while the corrosion was localized for the stainless steel muffler. Because aluminized carbon steel is perforated in a short time, most of today's mufflers are made of stainless steel.

When the automobile is driven over a long distance for a long period of time, the exhaust gas temperature exceeds 100°C so that moisture in the exhaust gas does not condensate in the muffler. When the automobile is run over a short distance for a short period of time, the exhaust gas temperature does not rise so high, resulting in the formation of exhaust gas condensate in the low-



(a) Aluminized carbon steel (b) Stainless steel (SUS410)

Photo 2 Corrosion conditions of mufflers in field automobiles

Table 2 Composition of exhaust gas condensate(mol/*l*)

Exhaust gas condensate	Cl^- $\times10^{-3}$	SO_4^{2-} $\times10^{-3}$	CO_3^{2-} $\times10^{-3}$	NO_3^- $\times10^{-3}$	NH_4^+ $\times10^{-3}$	Fe^{3+} $\times10^{-3}$	pH
①	0.69	0.82	2.8	1.6	8	3.1	8.1
②	2.80	2.6	9.8	1.6	54	2.5	8.4

Organic acids are contained in small amounts.

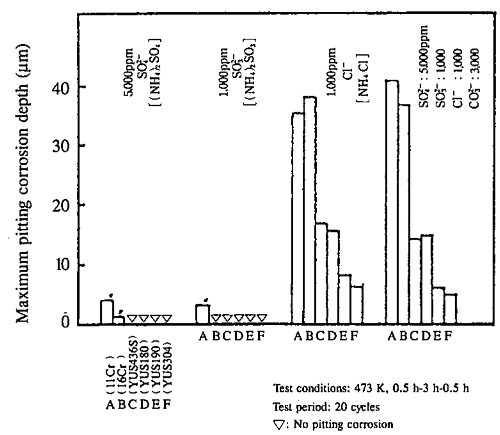


Fig. 10 Effects of anion species on localized corrosion of stainless steels in condensate environment

temperature area of the muffler. The condensate contains NH_4^+, CO_3^{2-}, SO_4^{2-}, Cl^- and organic acids, and has a pH value of about 8 to 9, as shown in **Table 2**[19]. Corrosion by this condensate is a problem for stainless steel mufflers.

Stainless steel specimens were partially immersed and heated in solutions to which were added 1,000 to 5,000 ppm of condensate components and were tested for the depth of pitting corrosion. The test results are given in **Fig. 10**. The pitting corrosion of mufflers is observed only in such an environment that chloride ions are also present. This means that chloride ions are a major contributor to localized corrosion[20]. The exhaust gas condensate is usually high in pH and environmentally mild. As the internal temperature of the muffler rises, the change of composition of the condensate is accelerated.

A certain amount of a simulative condensate of the composition given in **Table 3** was heated in a beaker to 50 to 500°C, and the condensate components left in the beaker were analyzed. The results are presented in **Fig. 11**[19]. The pH value declined with increasing heating temperature and was about 2 at about 473 K. Chloride ions dropped to several ppm at 200°C and were nearly extinct at higher temperatures. Sulfate ions remained at temperatures of up to 300°C. The region II of **Fig. 11** where Cl^- and SO_4^{2-} coexist is presumed to affect the localized corrosion of stainless steel. The data of **Fig. 11** suggest the following: When the automobile is driven continuously at high speed, corrosive substances have only a small possibility of remaining in the muffler, and corrosion is difficult to occur in the muffler. When the automobile is run over short distances for short periods of time, the repeated starts and stops gradually concentrate Cl^- and SO_4^{2-} in the condensate, and cause the localized corrosion of the muffler.

The dip and dry test method[21], partial immersion test method[22-24], and thermal and humidity cycling test method[23,25] are proposed as stainless steel evaluation methods that take into account the actual service conditions. Nippon Steel proposed the partial immersion and thermal cycling test method (hereinafter referred to as the NSC test method) that takes into account the above-mentioned changes in the conditions of the actual service environment[19]. The NSC test method is schematically illustrated in **Fig. 12**. The condensation and humidity conditions in the muffler are simulated by keeping the specimen partially immersed in the condensate. The corrosion of the muffler is simulated by holding the heating temperature at 130°C in the region II of **Fig. 11** and by moving the condensate level up and down in each cycle. The thermal cycle consisted of heating to 130°C for 30 min, holding at 130°C for 4 h, and cooling for 30 min. The standard simulative condensate composition was as given in **Table 4**.

Chromium and molybdenum additions are effective in retarding the localized corrosion of stainless steel in the exhaust gas condensate[18]. The changes in the pitting corrosion depth of chromium-molybdenum steel and commercial stainless steels as determined by the NSC test method are shown in **Figs. 13** and **14**, respectively. Before the warranty system was inaugurated, the 19Cr grade (YUS180) was used as material with high corrosion resistance. According to the findings discussed above, the YUS436S listed in **Table 1** was developed. YUS436S has the following characteristics: 1) its chromium and molybdenum contents can be optimized to inhibit the initiation and propagation of pitting corrosion that governs the muffler life; 2) it can be manufactured with high productivity by a highly efficient carbon steel production process (composed of tandem mill cold rolling, continuous annealing and descaling) by adding titanium in place of niobium; and 3) its chemical composition can be optimized to improve drawability and other forming properties. Today, YUS436S is widely applied as material for exhaust system components. Review of service performance requirements made from the point of view of optimal material selection and minimum material cost resulted in the development of a new YUS432 (17%Cr-0.5%Mo-Ti steel), which is now in commercial production.

The outside surface of the muffler is exposed to a corrosive environment and is coated with aluminum for appearance and corrosion protection. When YUS409D, YUS432 and YUS436 are aluminized, chromium in the base steel is imparted in trace amounts to the aluminum coating. This trace chromium proves very effective in improving the corrosion resistance of the aluminum coating itself (composed of the aluminum layer and alloy layer) and in enhancing the sacrificial protection of the base steel by the aluminum coating[26].

Muffler materials have rapidly changed from aluminized carbon steel to stainless steel from the standpoint of service performance such as corrosion resistance and service life warranty. At present, the shift to lower-cost materials is seen as a result of review made over the service performance of YUS436S. Given the safety and service life warranty requirements, muffler materials with present levels of service performance are believed to be necessary in the future, too. Mufflers will increase in size and geometrical complexity to meet tougher automotive noise regulations, to provide exhaust noise control, and to reduce the exhaust pressure loss. These trends will call for muffler materials with still better formability and weldability.

Table. 3 Composition of simulative exhaust gas condensate

pH	Cl^-(mol/l)	SO_4^{2-}(mol/l)	CO_3^{2-}(mol/l)	NH_4^+(mol/l)	NO_3^-(mol/l)
8.86	2.81×10^{-2} 1,000ppm	5.21×10^{-2} 5,000ppm	5.0×10^{-2} 3,000ppm	2.07×10^{-1} 3,740ppm	1.61×10^{-3} 100ppm

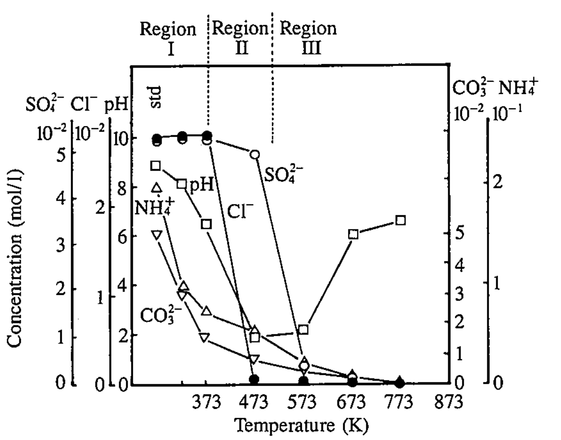


Fig. 11 Effect of temperature on condensate composition change in muffler

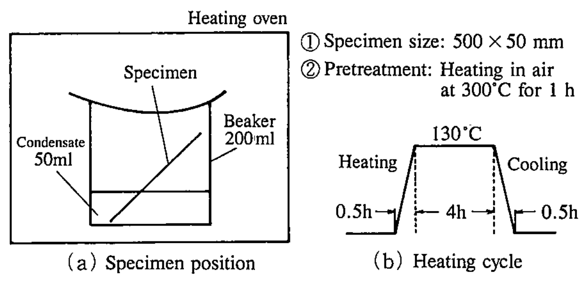


Fig. 12 Schematic diagram of NSC test method

Table 4 Composition of simulative test solution used in NSC test method (ppm)

pH	Cl^-	SO_4^{2-}	CO_3^{2-}	NO_3^-	NH_4^+	HCOOH
8.5	50	100	500	—	220	—

pH: Adjusted with NH_4OH
Each added in form of ammonium salt

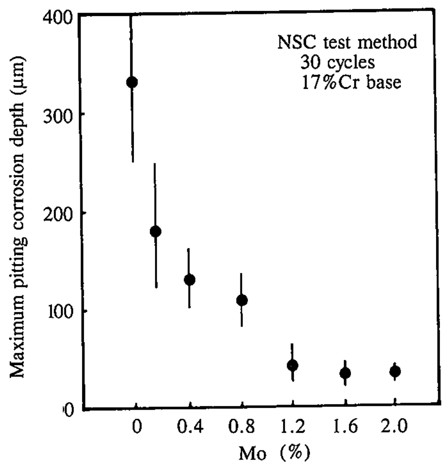


Fig. 13 Pitting corrosion depth of chromium-molybdenum steel by NSC test method

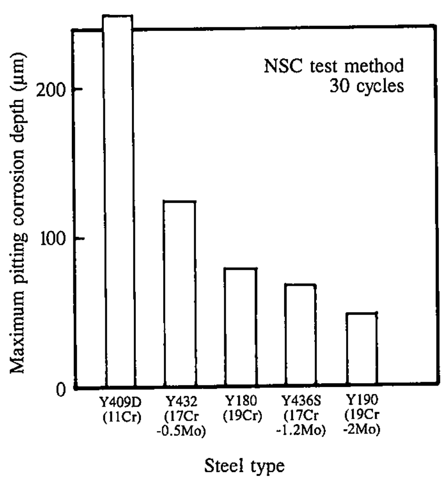


Fig. 14 Pitting corrosion depth of commercial stainless steels by NSC test method

3. Conclusions

Now, the application of stainless steel to exhaust system components is gradually taking root. The use of right materials in right applications will proceed with considerations given to balance between overall performance improvement, including formability and weldability, and cost. At the same time, the use of stainless steel in automobiles is expected to keep increasing to meet a variety of new regulations and social needs. Nippon Steel will push forward with its material development plan to make the most of the properties of stainless steels in enhancing automobile safety and performance, and will develop higher-performance materials with higher cost effectiveness in discharging its social responsibility as a material manufacturer.

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