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New Ferritic Stainless Steels in Automotive Exhaust System for Clean Environment

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Abstract

Recently, it is getting more important to consider global warming. Regarding automobiles, both to improve fuel economy and to clean exhaust gas are the most important issues to be solved. For these improvements, it is necessary to achieve lighter weights and higher exhaust gas temperatures. Therefore, materials for this use should have excellent heat resistance. In this paper, the materials for exhaust manifolds and catalytic converters, both of which are very important parts in exhaust systems to clean the exhaust gas, are introduced. Materials for the exhaust manifolds have been designed by the addition of Nb, Ti and Mo for stabilizing microstructures during high temperature service, thereby prolonging thermal fatigue life and improving hot-corrosion resistance. Regarding foil materials for the catalytic converter honeycomb, Fe-Cr-Al-Ln system, which has excellent oxidation resistance, has been selected as the foil material. Although this is very difficult to produce, it has been possible to produce using a normal commercial production line.

1. Preface

Prevention of air pollution and reduction of CO_2 emission are strongly required these years due to the rising general consciousness of global environment. Clean automobile exhaust gas and improvement of fuel consumption are being pursued in this context. It is necessary to raise the exhaust gas temperature and cut the body weight to attain these objectives. Exhaust manifolds suffer high temperature exhaust gas and catalytic converters (see **Fig. 1**) contribute to the cleaning of exhaust gas at high temperature, which requires that these parts have excellent heat resistance. A number of new materials have been developed for the exhaust system components[1-6]. This report describes alloy design concepts of the materials for the exhaust manifold and the catalytic converter and the products developed for these applications.

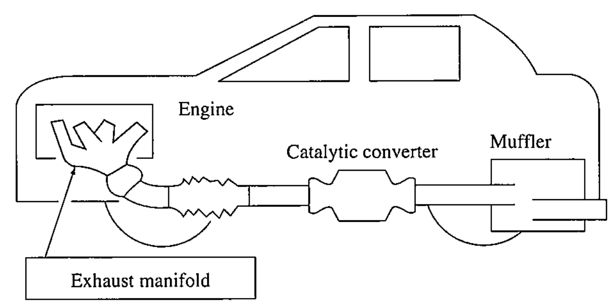

Fig. 1 Schematic illustration for automobile exhaust system

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2. Development of Materials for the Exhaust Manifold

2.1 Stainless steel manifold contributing to clean exhaust gas and vehicle weight reduction

The exhaust manifold directly suffers high temperature exhaust gas (**Fig. 1**) and effectively vents the exhaust gas to the catalytic converter utilizing the exhaust interference effect between the cylinders. Because of the complex shape, it has been manufactured conventionally by cast iron. Due to the latest legal regulations demanding more stringent control of the exhaust gas, it became extremely important to clean exhaust gas as quickly after the start of the engine as possible (cold start measures). This requirement comes from the fact that the efficiency of a catalytic converter is low while its temperature is low soon after the engine start and hazardous ingredients in the exhaust gas (NO_x, hydrocarbon, etc) are discharged in quantities during this phase. Hence, it is important to raise the exhaust gas temperature (approximately over 900°C) and lower the heat capacity of the exhaust system by the use of thinner materials in order to send high temperature exhaust gas to the converter keeping its temperature as high as possible so that the catalyst is quickly heated up to the active temperature range.

Enhancement of heat resistance and reduction of thickness of the material became envisaged for the above reasons and consequently the cast manifolds began to be replaced with those made of conventional stainless steel sheets or tubes such as type 409 (Nippon Steel Standard YUS409D: 11Cr-Ti), JIS SUS430J1L (Nippon Steel Standard YUS180: 19Cr-Nb), etc[7]. Today various types of heat resistant ferritic stainless steels have been developed and commercially applied[1-6, 8-10]. These newly developed steels are given different heat resistance for coping with various engine types of different exhaust gas temperatures.

2.2 Required properties and effects of alloying elements

The exhaust manifold undergoes thermal fatigue of heating and cooling imposed by the travelling pattern of the vehicle. The maximum temperature varies according to the engine type but it is said to go up to approximately 900°C. For this reason, the material is required to withstand oxidation and deformation at high temperatures. The life of the parts is affected especially by thermal fatigue of the material. Thermal fatigue of sheet products can lead to rupture of the sheet constructions through local strain concentration caused by constraint of thermal expansion. It is important, therefore, to minimize thermal strain and hence, the materials are required to have low thermal expansion and high strength at high temperatures. For this reason the guideline for the alloy design is to enhance strength at high temperatures of ferritic stainless steels, which have low thermal expansion[11]. In addition, resistance against aging deterioration (loss of strength after prolonged high temperature use) and hot corrosion by chloride is important for allowing the use of thinner materials. Oxidation resistance at the service temperature and formability are also required.

2.2.1 High temperature strength of ferritic stainless steels

Fig. 2 shows effects of alloying elements on the 0.2% offset yield strength at 950°C of ferritic stainless steels. Addition of Nb, Mo, W and Ta are effective for improving high temperature strength and especially Nb, shows a remarkable effect with a small amount of addition. It was discovered that it is effective for enhancing the high temperature strength to maintain the solid solution amounts of Nb and Mo[8]. The guideline for alloy design is, therefore, to fully utilize solute Nb and Mo.

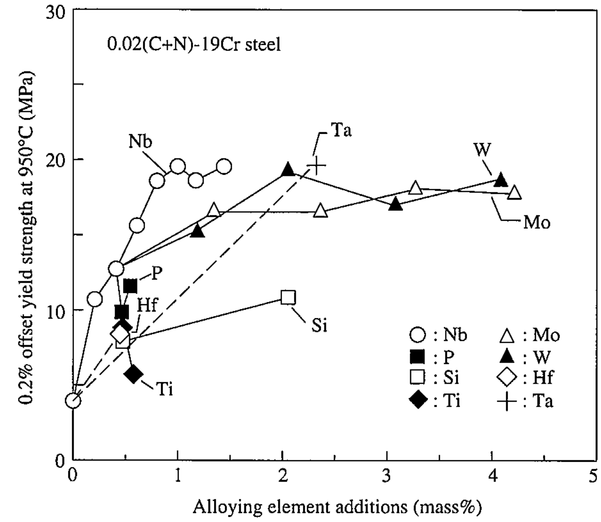

Fig. 2 Effects of element additions on the 0.2% offset yield strength at 950°C of 19Cr ferritic stainless steel

2.2.2 Prevention of aging deterioration and improvement of thermal fatigue properties

It is well known that Nb has a strong affinity with C and N while being effective for enhancing the high temperature strength. **Fig. 3** shows change of precipitates of Nb-added and Nb-Ti-added 13Cr ferritic stainless steels after aging at 900°C. In the Nb-added steel carbides became coarse after aging, consuming solute Nb while, in the Nb-Ti-added steel, Fe_2Nb precipitates during aging but it was not as coarse as carbide in the Nb-added steel and the consumption of the solute Nb during the precipitation was not so large.

Fig. 4 shows change of high temperature strength of the Nb-added and Nb-Ti-added steels by aging, both the steels having the same initial high temperature strength at 900°C. The Nb-Ti-added steel shows smaller loss of high temperature strength through aging than the Nb-added steel. This is because precipitation of coarse Nb carbide (M_6C) was hindered by the addition of Ti[8]. Consequently, it was discovered that for maintaining the high temperature strength for a long period, it was especially effective to add Ti in combination and this also contributed to improvement of thermal

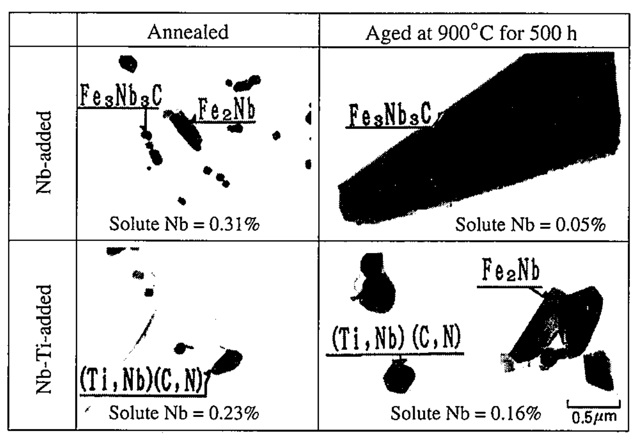

Fig. 3 Change of precipitates and solute Nb of Nb-added and Nb-Ti-added 13Cr ferritic stainless steels under aging at 900°C

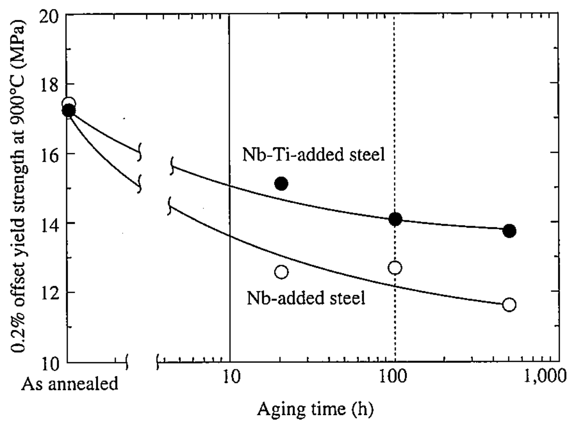

Fig. 4 Change of the 0.2% offset yield strength at 900°C of Nb-added and Nb-Ti-added steels under aging at 900°C

fatigue life[8]. As for Mo, it has been reported that it does not precipitate at temperatures above 900°C[8,9], and does so in the form of the Laves phase (Fe_2Mo type) in lower temperatures[12].

2.2.3 Enhancement of hot corrosion resistance by chloride

Thickness loss by hot chloride corrosion was calculated from the weight loss after a corrosion test with the assumption that the loss occurred homogeneously, and the value thus obtained was used as an index of the hot corrosion resistance by chloride. **Fig. 5** shows effects of Mo on the hot corrosion resistance by chloride of 13Cr ferritic stainless steels. The addition of Mo was found to improve hot corrosion resistance by chloride. The effects of Mo begins to show with an addition of only 0.5% and it is larger at the higher service temperature range.

2.3 Nippon Steel's ferritic stainless steel products for exhaust manifold

From the above discussions, under a design guideline that additions of Ti, Nb and Mo would be the principal method, new ferritic stainless steels were developed having high temperature strength suitable for different service temperature ranges as well as thermal fatigue life and hot corrosion resistance properties. **Table 1** shows the mechanical properties of the developed products, i.e., YUS409D (11Cr-Ti) for low temperature use, YUS450MS (14Cr-Ti-0.3Nb-0.5Mo) for high temperature use and YUS190EM (19Cr-Ti-0.5Nb-2Mo) for higher temperature use, and **Figs. 6** and **7** show their high temperature strength and thermal fatigue properties, respectively. Compared with the Nb-added JIS SUS430J1L and Nippon

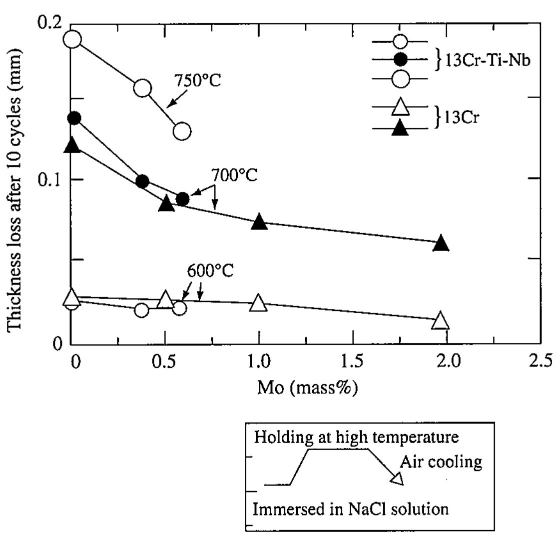

Fig. 5 Effects of Mo on thickness loss of 13Cr ferritic stainless steel by hot corrosion damage with chloride

Table 1 Mechanical properties of the new stainless steel materials for exhaust manifold

Denomination	YUS409D 11Cr-Ti-LC	YUS450MS 14Cr-Ti-0.3Nb-0.5Mo-LC	YUS190EM 19Cr-Ti-0.5Nb-2Mo-LC
Yield strength (N/mm^2)	235	295	330
Tensile strength (N/mm^2)	430	470	525
Elongation (%)	35	32	30
$\bar{r}$-value (gauge = 2.0 mm)	1.5	1.3	1.1

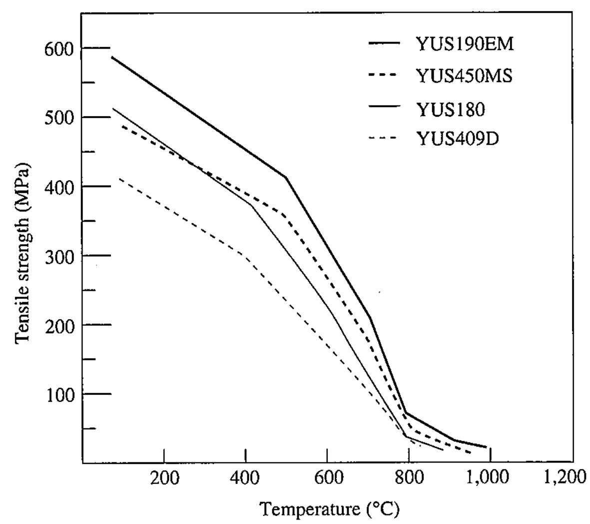

Fig. 6 Comparison of high temperature strength of exhaust manifold materials

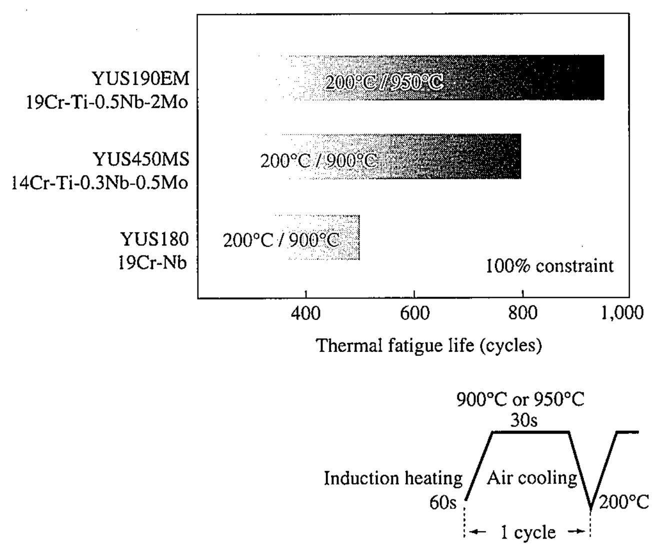

Fig. 7 Comparison of thermal fatigue life of exhaust manifold materials

Steel Standard YUS180 (19Cr-Nb), the Nb-Ti-Mo-added YUS450MS has a longer thermal fatigue life. YUS190EM for higher temperature use has longer life than YUS180 and YUS450MS under a temperature cycle range from 200°C to 900°C despite its maximum service temperature of 950°C.

3. Development of Foil Materials for Catalytic Converters

3.1 Foils for catalytic converters for maximum utilization of exhaust gas cleaning capacity

Some catalytic converters are installed beneath the floor panel as shown in **Fig. 1** and others immediately after the exhaust manifold in order to clean gas as soon as possible after engines start. Construction of the converter is shown in **Fig. 8**. It comprises an outer shell and a honeycomb and the catalyst (γ-alumina and some noble metal) covers the honeycomb surface. The honeycomb was conventionally made of ceramics, but if changed to metal advantages such as a lower pressure loss, smaller heat capacity resulting in shorter time required for heating up the catalyst to the active temperature, etc. could be expected. For this reason, metal honeycomb was first used in Germany in the mid 1980's[13], and it is used now in developed countries.

3.2 Properties required of the foil materials and effects of the steel chemistry

Especially excellent oxidation resistance is required of the honeycomb materials as they are used in the form of foils as thin as 30 - 50 μm. Adhesion of oxidized layer has to be considered in order to prevent the catalyst from peeling off. Resistance against thermal stress is also important as the outer shell and the honeycomb expands and shrinks due to heating and cooling during acceleration/deceleration of the vehicle in motion. The alloy design would therefore be that the material should be ferritic stainless steel, which has a small thermal expansion, and have a high oxidation resistance and good adhesion of the oxidized layer.

3.2.1 Enhancement of oxidation resistance of the foil

From the viewpoint of oxidation resistance, the Al_2O_3 film on Fe-Cr-Al stainless steels is superior to the Cr_2O_3 film on ordinary Fe-Cr steels. **Fig. 9** shows comparison of oxidation resistance properties between Fe-Cr steel (19Cr-Nb) and Fe-Cr-Al steel (15Cr-4Al). The 15Cr-4Al steel shows far smaller weight gain during holding time at high temperatures than the 19Cr steel, and proves to have superior oxidation resistance in spite of its low Cr contents. This is because the diffusion rate of Al ion or O ion in the Al_2O_3 film is lower than that of Cr ion in the Cr_2O_3 film. **Fig. 10** shows effects of Cr-Al amount on the oxidation resistance of the foil in the exhaust gas atmosphere. The oxidation resistance increases as the amounts of Al and Cr are increased, but due to production process limitation the Al-addition amount is limited approximately to 5% in weight at the maximum[14]. A practical and satisfactory level of oxidation resistance is obtained when Cr content is larger than 20% in weight.

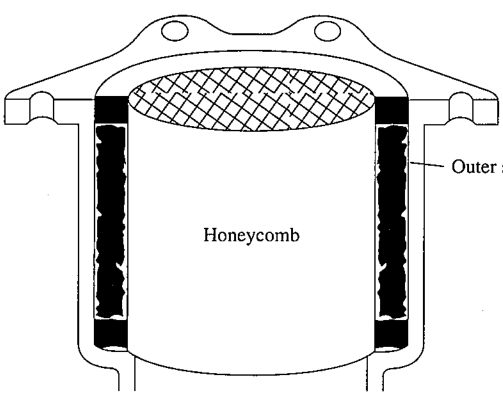

Fig. 8 Schematic illustration for construction of catalytic converter

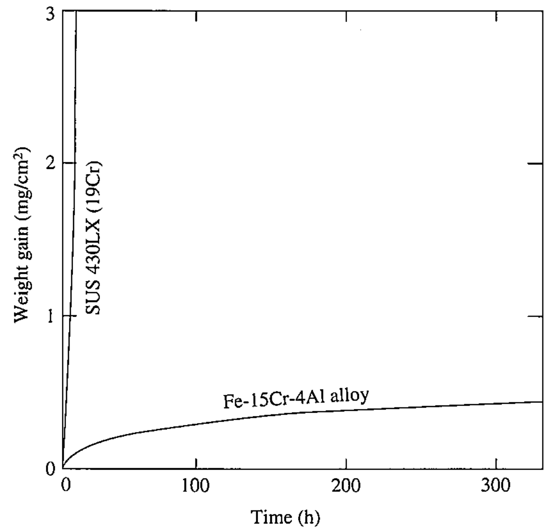

Fig. 9 Weight change of 19Cr and 15Cr-4Al steels under atmospheric oxidation test at 1,100°C

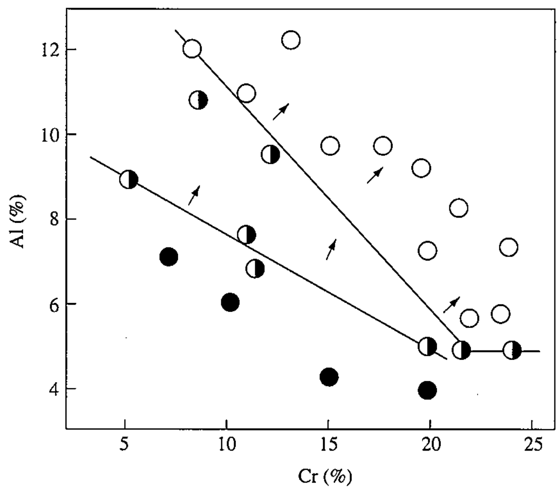

Fig. 10 Effects of Cr-Al amounts on the oxidation behavior of a foil (50 μm thick) in automobile exhaust gas

3.2.2 Enhancement of adhesion of oxidation film

It is known that addition of rare earth elements such as Y, Sc, etc. is effective for enhancing adhesion of the oxidation film[15]. Among the rare earth elements lanthanoid (Ln: mixture of rare earth elements such as Ce, Pr, Nd, etc. excluding Y and Se) is inexpensive.

Fig. 11 shows change over time of oxidation weight gain of 20Cr-5Al steels added with different quantities of Ln under an

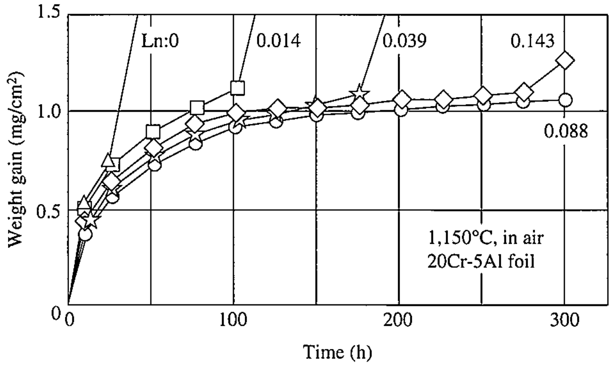

Fig. 11 Effects of Ln amount on the intermittent oxidation behavior of 20Cr-5Al steel in the atmosphere

intermittent oxidation test [16]. Generally speaking, when a protective oxidation film such as Al_2O_3 is formed, the relation between oxidation weight gain and time follows the 1/n-th rule (n being an integer). A deviation from this exponential rule is called "breakaway" meaning loss of protection and adhesion of the oxidation film due to local progress of oxidation. The time to the breakaway is made longer when the Ln addition is increases as long as the Ln amount is 0.088% or less, but when the Ln amount is over 0.1% the breakaway occurs in a short period instead. In order to utilize the film adhesion effects by the Ln-addition, therefore, the amount of Ln has to be limited to 0.07 - 0.09%. In this range the oxidation film formation mechanism inhibits Al ion diffusion and thus O ion diffusion becomes predominant. This reduces formation of voids between the metal and the film and the stress inside the film, resulting in improved film adhesion.

3.3 Nippon Steel's foil for catalytic converters

Based of the above discussions, YUS205M1 (20Cr-5Al-0.08Ln) was developed as a foil product for catalytic converters and its production on conventional stainless steel production lines was made possible as the first case in the world, despite difficulties[15, 17].

4. Future Prospects

General environment consciousness has increased and the trend is that regulations of automobile exhaust gas are becoming increasingly stringent in the Unite States and other countries in the world. Under such a trend, currently used exhaust manifolds and catalyst carriers may become unsuitable in some cases in the cold start situations. It is essential to further reduce the hazardous elements in the exhaust gas by fully utilizing the catalytic activities from the phase immediately after the start of the engines. As a response, things such as double tube manifolds and thinner honeycomb materials are being tried. Further, the exhaust gas regulations hitherto applied mainly to four-wheeled gasoline-powered vehicles are being extended to motorcycles and diesel engine vehicles. In this background, further exhaust gas-cleaning measures through expanded use of stainless steels for the exhaust system and application of stainless honeycomb to the catalytic converters will be pursued and it is expected that stainless steels will find wider applications.

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