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Technical Report

Development of Heat Resistant Stainless Steel NSSC® 21M for Catalysis Substrate of Motorcycle Muffler

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Abstract

Recently, the number of motorcycles equipped with catalyst for purifying exhaust gas is increasing. In some motorcycles, catalyst slurry is directly pasted onto the surfaces of the muffler components to reduce cost. In this case, oxidation resistance is required for materials used for the muffler components to prevent deterioration of catalyst. SUH21 (18Cr-3Al) is one of the most common materials used for this particular application by utilizing its excellent oxidation resistance. However, its insufficient formability sometimes reduces productivity of motorcycle mufflers and there is an intense need for materials with improved formability and good high-temperature performance. To develop a new stainless steel having excellent oxidation resistance and formability, influences of Al and Si additions to high-purity 18Cr-Ti ferritic stainless steel on oxidation resist-ance and formability were investigated. The optimum contents of Al and Si are 2mass% and 0.5mass%, respectively, resulting in a finalized chemical composition of 18Cr-2Al-0.5Si-Ti. This newly developed stainless steel NSSC 21M for catalyst substrate has excellent oxidation resistance equivalent to conventional SUH21 and formability better than SUH21. It has in fact been used for mufflers in more than 100,000 motorcycles so far.

1. Introduction

Regulations on exhaust gas from motorcycles, as well as four-wheeled vehicles, are becoming increasingly stringent.[1] Accordingly, more and more motorcycles are being fitted with catalysts to purify exhaust gas. Many of those motorcycles are equipped with catalytic converters similar to those in four-wheeled vehicles. However, there are cases in which the catalyst is directly applied to the inner surface of the motorcycle muffler. The muffler of a motorcycle is schematically shown in **Fig. 1**. The catalyst is applied to the surfaces of the heat tube or the inner surface of the exhaust pipe. When a catalyst for purifying exhaust gas is used, the muffler interior can reach temperatures as high as 700℃ to 900℃ due to the heat of the catalyst reaction. At such high temperatures, oxidation of the muffler components is accelerated. When a catalyst is applied directly to SUS436L (17Cr-1Mo), which is a common material for mufflers, the Fe in oxide scale formed between the catalyst layer and the muffler component diffuse into the catalyst layer, causing a decline in the cata-

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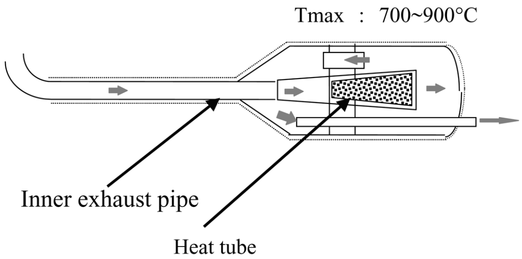

Fig. 1 Schematic illustration of the motorcycle muffler

lyst performance. Since it is necessary to restrain the diffusion of Fe in the catalyst layer, the catalyst-supporting material is required to have exceptionally high oxidation resistance.

In terms of stainless steels with superior oxidation resistance to SUS436L, there are Al-containing ferritic stainless steels as represented by SUH21 (18Cr-3Al).[2] When SUH21 is used for the muffler components, the catalyst does not deteriorate since a dense film of Al_2O_3 is formed on the component surface. This is due to the amount of Fe contained in the Al_2O_3 film being so small that Fe is not diffused in the catalyst layer. In contrast, since the formability of SUH21 is inadequate, the formability of the base metal and welds that are important in the process of shaping a muffler is also rather poor. Therefore, when SUH21 is used as a material for mufflers, it can invite certain problems, such as a decline in yield in muffler production.

If an Al-containing ferritic stainless steel with comparable oxidation resistance to SUH21 but with superior formability of the base metal and welds were available, it would be an ideal material for catalyst-supporting mufflers.

Under this premise, we sought the creation of a new Al-containing ferritic stainless steel that has both excellent oxidation resistance and formability. As a result, we formulated NSSC 21M—a new stainless steel grade.[3, 4]

2. Concept of Alloying Design

Aluminum is an element which, when added to a steel, improves the oxidation resistance of the steel but, at the same time, reduces the formability of the steel. In order to obtain both excellent oxidation resistance and excellent formability, it is important to minimize the Al content as much as possible, since it is undesirable from the standpoint of formability, while securing the required oxidation resistance by using an 18Cr steel as the base. In addition, we decided to minimize the C and N content as much as possible so as to ensure the required formability and to add Ti so as to fix C and N in the form of carbides and nitrides. Therefore, in the present development, we discussed 18Cr-Al-Ti steels.

3. Experimental Method

3.1 Specimens

The chemical compositions of the steels tested are shown in **Table 1**. Those steels were melted in a vacuum melting furnace and made into 20-kg steel ingots. Then, each of the steel ingots was hot-rolled, cold-rolled, annealed and made into 1.2-mm thick sheets, which were tested as described below.

3.2 Oxidation resistance

In the present development, we conducted an oxidation test in an actual exhaust gas atmosphere containing 1% oxygen and 10% moisture. The test temperature was varied from 600℃ to 1,100℃, and the test time was 5 hours. The oxidation test was conducted in such an exhaust gas atmosphere because the behavior of steel oxidation in the actual exhaust gas atmosphere can differ markedly from that in the open atmosphere. After the oxidation test, the oxidation gain in weight of each specimen was measured and the appearance of each specimen was observed. In addition, to analyze the structure of the oxide film, samples for cross-sectional observation were prepared from some specimens using the focused ion beam (FIB) method and observed under a field emission-type transmission electron microscope (FE-TEM).

3.3 Formability

Concerning the formability of the base metals, we conducted a tensile test using JIS 13B test pieces in accordance with the Japanese Industrial Standards (JIS) and evaluated the formability in terms of ductility. The test forces were applied in the rolling direction. The formability of welds was evaluated by subjecting the welds to an Erichsen test in accordance with JIS. The samples were prepared using tungsten inert gas (TIG) welding without filler and the welding conditions were 200A - 12 V - 180 cm/min.

4. Results and Discussions

4.1 Oxidation resistance

Fig. 2 shows the influence of the Al content on the oxidation gain in weight of steel measured in the oxidation test in the exhaust gas atmosphere.[5] The Si content of the steels tested was 0.1 mass%. As the figure shows, when the test temperature is 800℃ or higher, the oxidation gain in weight reaches a peak at an Al content of approximately 1 mass% and then declines sharply with the increase in Al content to become stably low at an Al content of 2 mass% or more.

Fig. 3 shows the results of TEM observation of the cross section of a 1Al sample oxidized at 800℃.[6] Together with the bright field image and the results of an analysis using the micro-region energy

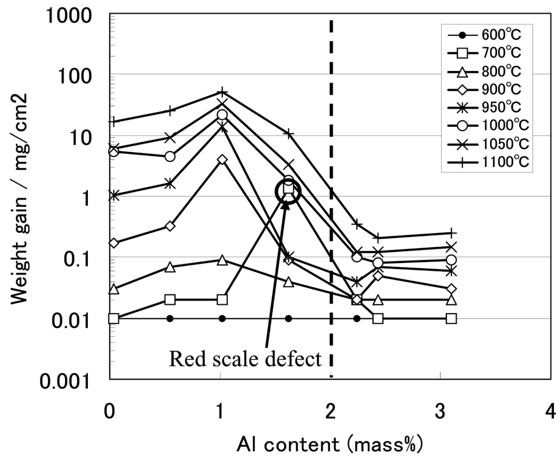

Fig. 2 Al content dependence of weight gain after oxidation test in an exhaust gas atmosphere for 5h

Table 1 Chemical compositions of tested steels (mass%)

C	Si	Mn	P	S	Ni	Cr	Al	Ti	N
0.005	0.1 - 1.5	0.2	0.02	0.003	0.1	18	0.04 - 3.1	0.05 - 0.15	0.008

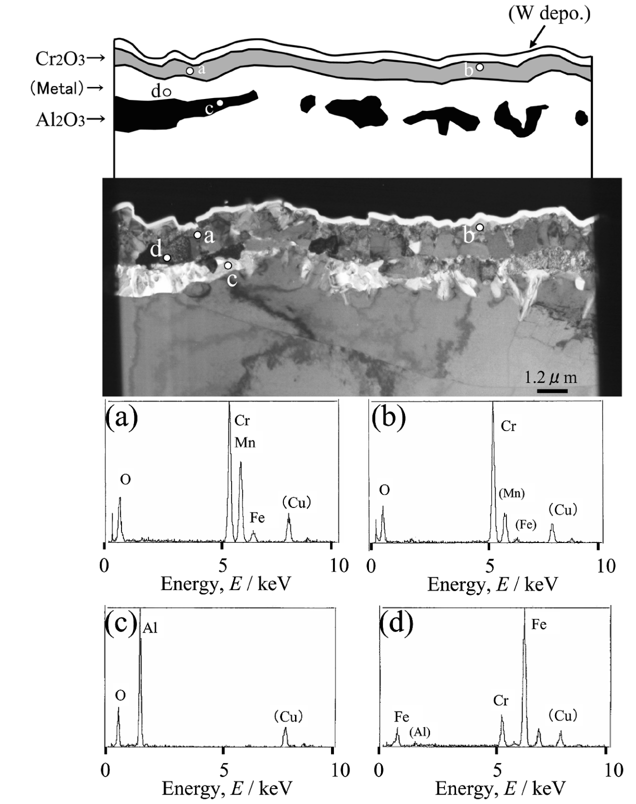

Fig. 3 TEM observation results of cross sectional view of 1Al sample oxidized at 800℃

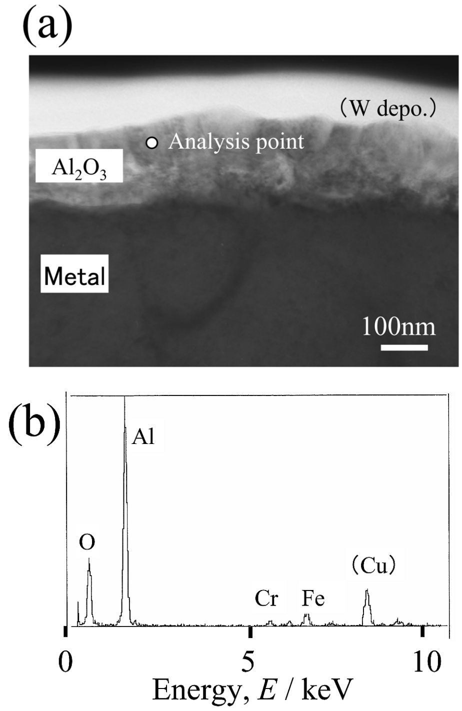

Fig. 4 TEM observation results of cross sectional view of 2Al sample oxidized at 800℃

dispersion-type X-ray spectroscopic method (μ-EDS), the scale and neighboring structure are also shown schematically. When the Al content is not more than approximately 1 mass%, a protective scale of Al_2O_3-based oxide film is not formed: the topmost layer of the protective scale is a Cr_2O_3-based oxide film, while Al forms an internal Al oxide layer underneath the topmost layer. The internal Al oxide layer is not completely continuous, although it appears more or less continuous. A metal layer—the parent phase—is observed between the Cr_2O_3-based oxide layer and the internal Al oxide layer.

Fig. 4 shows the results of TEM observation of the cross section of a 2Al sample oxidized at 800℃.[6] Fig. 4 (a) shows a bright field image. The white topmost layer is a tungsten layer that was deposited to protect the scale during the forming by FIB. A uniform scale layer about 100-nm thick has been observed underneath the tungsten layer. Fig. 4 (b) shows the results of a μ-EDS analysis of the scale layer. With the exception of Al, metallic elements are almost nonexistent, and an Al_2O_3 film containing few impurities has been formed as the topmost layer of the sample. From this, the decrease in oxidation gain in weight at an Al content of 2 mass% or more is considered attributable to the formation of the Al_2O_3-based film.

The protective scale formed when Al is not added is Cr_2O_3 film, whereas it is Al_2O_3 film when the Al content is 2 mass% or more. When the Al content is between 0 and 2 mass%, the protective scale gradually changes from Cr_2O_3 film to Al_2O_3 film with the increase in Al content. On the low-Al side, with the increase in Al content, the internal Al oxidation increases, making the internal Al oxide layer continuous. As the layer becomes continuous, the diffusion of metallic elements from the inside of the mother phase is restrained. As a result, the Cr_2O_3 film that is formed by outward diffusion of the metallic elements becomes Cr-deficient, and Mn, Fe and other metallic elements are oxidized. Therefore, the oxidation resistance of the oxide film decreases and the oxidation gain in weight increases. The above process occurs when the Al content is not more than 1 mass%.

When the content of Al is increased beyond 1 mass%, the internal Al oxide layer becomes continuous, whereby the oxidation resistance improves and the oxidation gain in weight is restrained. In addition, when the Al content continues to increase further, the oxidation of Al becomes more prevalent than the oxidation of Cr, eventually causing the formation of an Al_2O_3 oxide film on the topmost layer, rather than the internal Al oxidation.

Fig. 2 shows that the oxidation gain in weight of the Al 1.6 mass% sample oxidized at 700℃ is unusually large. This is due to the formation of a Fe oxide called red scale. It has been confirmed that the formation of red scale at 700℃ occurs in an exhaust gas atmosphere but does not occur in the open air.[6] In other words, 700℃ is the most grueling temperature condition for oxidation resistance of motorcycle muffler material in an exhaust gas atmosphere. Thus, we found that in the development of a new muffler material, it was necessary to secure excellent oxidation resistance at 700℃, that is, restrain the formation of red scale.

To restrain the formation of red scale, we studied the effect of Si addition to steel on red scale formation. **Fig. 5** shows the effects of Al and Si on the formation of red scale in an oxidation test conducted in an exhaust gas atmosphere at 700℃ for 5 hours.[7] The figure shows that red scale occurs in a very narrow region around the Al content of 1.6 mass% indicated by the dotted lines in Fig. 5, and that the formation of red scale can effectively be restrained by adding 0.5 mass% Si.

The samples containing 2 mass% Al were free of red scale. Observed under a scanning electron microscope (SEM), they seemed to have a thin, dense Al_2O_3 film formed on the surface. It was found,

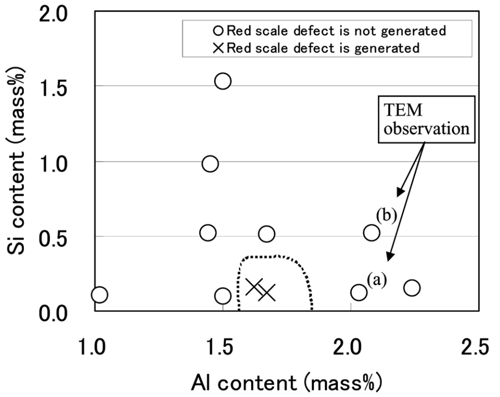

Fig. 5 Effects of Al and Si on the formation of red scale defects in an oxidation test in an exhaust gas atmosphere at 700℃ for 5h

however, that the addition of Si made a marked difference to the characteristics of the film. **Fig. 6** shows the results of TEM observation of the cross section of the oxide film formed on each of the samples of (a) 2Al-0.1Si steel and (b) 2Al-0.5Si steel, shown in Fig. 5, after an oxidation test. The bright field image (BFI) of each sample shows a very thin oxide film about 100-nm thick directly underneath the tungsten layer (white layer) that was deposited to protect the surface scale during the FIB working. However, the μ -EDS analysis results show that there is a marked difference in oxide film composition between the two samples. Namely, the oxide film formed on (a) 2Al-0.1Si steel contains large proportions of Fe and Cr, whereas the oxide film on (b) 2Al-0.5Si steel contains a large proportion of Al and only small proportions of Fe and Cr.

Thus, the oxide film on the 2Al-0.1Si steel contains many impurities and a dense Al_2O_3 film is absent. By contrast, on the 2Al-0.5Si steel, which contains a larger amount of Si, a dense Al_2O_3 film containing few impurities is formed. This favorable effect of Si addition is considered to be due to the following fact. Although Si is oxidized less easily than Al, it is oxidized more easily than Fe and Cr. Therefore, Al and Si are oxidized preferentially, whereby the oxidation of Fe and Cr is restrained. As a result, a dense Al_2O_3 film containing few impurities is formed.

The above discussions indicate that in order to obtain a dense Al_2O_3 film in an exhaust gas atmosphere at 700℃ which is the most grueling temperature condition for oxidation resistance, it is necessary to add not only 2 mass% Al but also 0.5 mass% Si to the steel.

4.2 Formability

Fig. 7 shows the effects of Al and Si on the elongation of steel. With the increase in Al content up to 3 mass%, the elongation gradually decreases. In contrast, even when the content of Si is increased up to 1 mass%, the elongation remains almost the same. However, when the Si content is increased to 1.5 mass%, the elongation decreases sharply. In other words, as long as the Si content is within 1 mass%, the elongation is almost unaffected.

Fig. 8 shows the results of an Erichsen test of welds and the effects of Al and Si on the Erichsen value of those welds. When the Al content is increased to 2.5 mass% and the Si content is increased to 1 mass%, the Erichsen value decreases sharply. This sharp decrease in Erichsen value is due to brittle cracking of the welds.

Based on the results of an oxidation test in an exhaust gas atmosphere and the results of discussions on the formability of the base metal and welds, we judged that 2 mass% Al and 0.5 mass% Si are the optimum combination to impart the desired oxidation resistance and

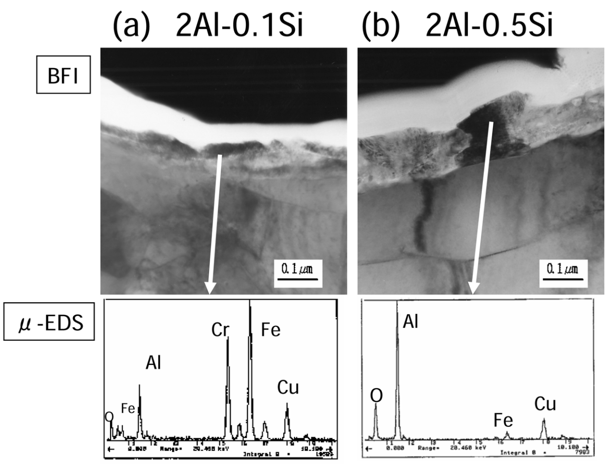

Fig. 6 TEM observation results in a cross-sectional view of samples oxidized at 700℃

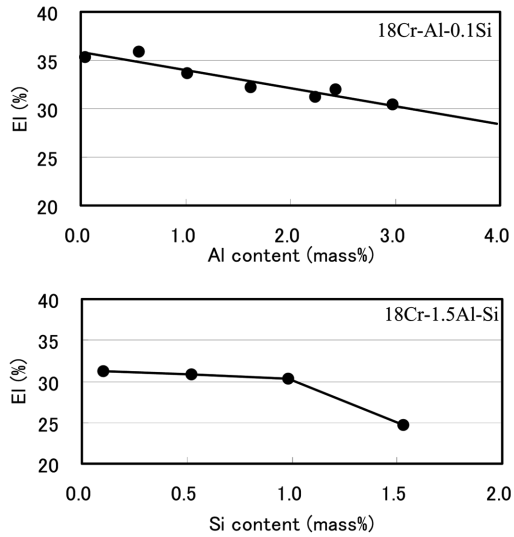

Fig. 7 Effects of Al and Si on elongation

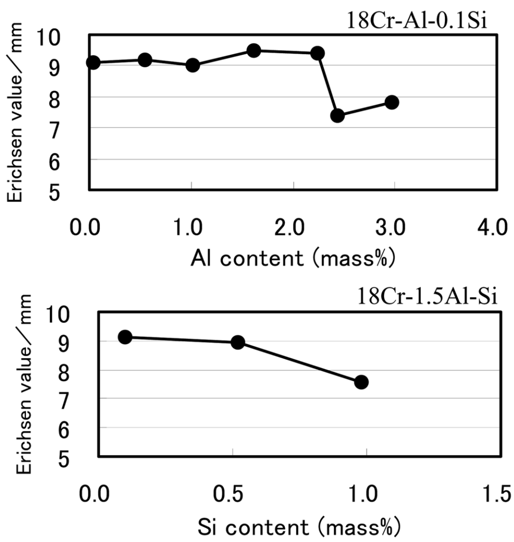

Fig. 8 Effects of Al and Si on the Erichsen values of welds

formability to the steel being developed. Therefore, we designated NSSC 21M as an 18Cr-2Al-0.5Si-Ti steel.

5. Properties of Newly-Developed NSSC 21M

Table 2 shows the representative chemical composition of NSSC 21M. As a reference, the typical chemical composition of SUH21 is also shown. Sample sheets of the two steels, each 1-mm thick, were used to compare their properties. Oxidation resistance was evaluated by subjecting the samples coated with catalyst to an oxidation test in the same exhaust gas atmosphere as described earlier. The oxidation test was conducted 10 times for each sample at 700℃ for 5 hours. **Fig. 9** shows the appearance of the samples after the oxidation tests. Both NSSC 21M and SUH21 did not change in appearance and their catalytic layer remained sound, indicating that they have nearly the same oxidation resistance.

Fig. 10 shows the base metal elongation in the rolling direction and the results of an Erichsen test of TIG welds for each sample. NSSC 21M is superior to SUH21 in terms of both elongation and Erichsen value. In particular, NSSC 21M has a high elongation, which is comparable to that of ordinary SUS436L (30% to 32%).

The above results indicate that NSSC 21M has both excellent oxidation resistance and excellent formability. NSSC 21M is already being used in the mufflers of many motorcycles, mainly scooters as shown in **Fig. 11**, and has demonstrated superb performance.

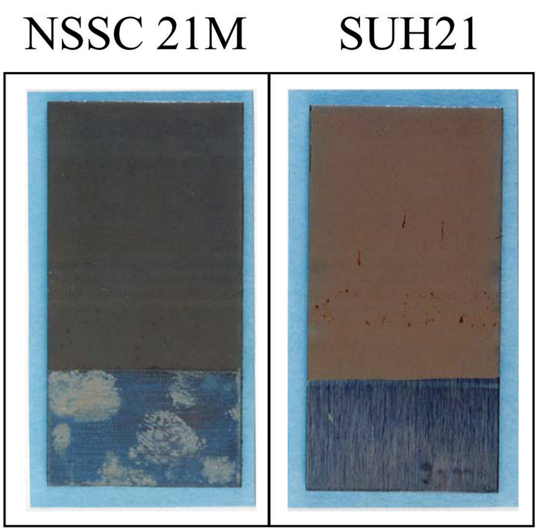

Fig. 9 Appearance of steels with pasted catalyst after an oxidation test (700℃, 5h, 10times)

Table 2 Examples of chemical compositions of NSSC 21M and SUH21

Steel	Chemical composition (mass%)								
	C	Si	Mn	P	S	Cr	Ti	N	Al
NSSC21M	0.0022	0.45	0.24	0.029	0.007	18.1	0.17	0.0065	2.1
SUH21	0.0080	0.25	0.22	0.032	< 0.0003	18.2	0.16	0.0080	3.1

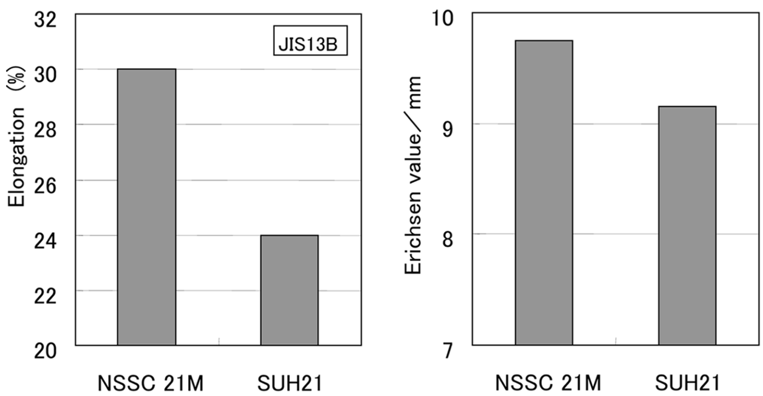

Fig. 10 Formability of NSSC 21M comparison with SUH21

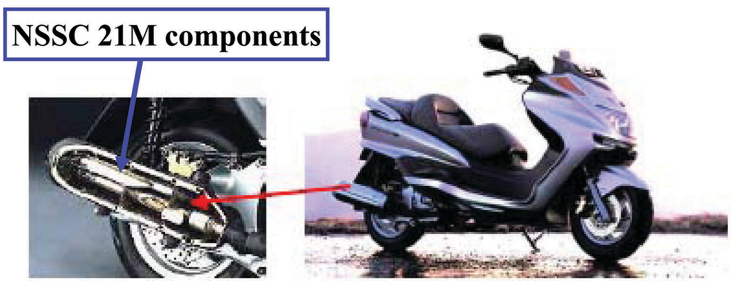

Fig. 11 Example of application of NSSC 21M

6. Conclusion

The test results we obtained are as follows.

(1) The oxidation gain in weight of steel in an oxidation test is restrained by the addition of Al of 2 mass% or more. This is attributable to the formation of an Al_2O_3 film.

(2) The oxidation resistance of steel improves with the addition of Si of up to 0.5 mass%. This is because the concentration of Fe, Cr and other impurities in the Al_2O_3 film decreases with the increase in Si.

(3) With the decrease in the amount of Al, the elongation of steel increases. When 2.5 mass% or more Al is added, the Erichsen value of welds decreases markedly.

(4) The elongation of steel does not change significantly when the amount of Si is not more than 1 mass%.

Based on the above test results, we judged that the optimum amount of Al and Si to be added was 2 mass% and 0.5 mass% respectively, and that the steel to be newly developed should be an 18Cr-2Al-0.5Si-Ti steel. Eventually, we formulated the new steel grade, NSSC 21M, as a catalyst supporter. This steel is comparable in oxidation resistance to SUH21 and superior in formability to SUH21. NSSC 21M has already been applied to the mufflers of more than 100,000 motorcycles.

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