DEVELOPMENT OF NEW ADVANCED STAINLESS STEEL FOR CATALYST SUBSTRATE OF MOTORCYCLE MUFFLER

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Abstract

Recently, the number of motorcycles equipped with a 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 the catalyst.

18Cr-3Al stainless steel 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 oxidation resistance equivalent to 18Cr-3Al and better formability than 18Cr-3Al, influences of Al and Si additions to high-purity 18Cr-Ti ferritic stainless steel, which has good formability, on oxidation resistance 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 for catalyst substrate has excellent oxidation resistance equivalent to conventional 18Cr-3Al and formability better than 18Cr-3Al. It has in fact been used for mufflers in more than 100,000 motorcycles so far.

Introduction

In recent years, to respond to tightened emission control[1], the number of motorcycles equipped with a catalyst for purifying exhaust gas is increasing. In many motorcycles, catalytic converters are used as in the case of four-wheeled vehicles. However, catalyst slurry is directly pasted onto the surfaces of the muffler components in some motorcycles to reduce cost. Figure 1 shows a schematic illustration of the motorcycle muffler. Catalyst slurry is usually pasted onto the surfaces of the heat tube and/or the inner surface of the inner exhaust pipe. The temperature of the muffler with a catalyst reaches 700 - 900ºC due to heat of catalysis. The muffler components are oxidized and oxide scale forms

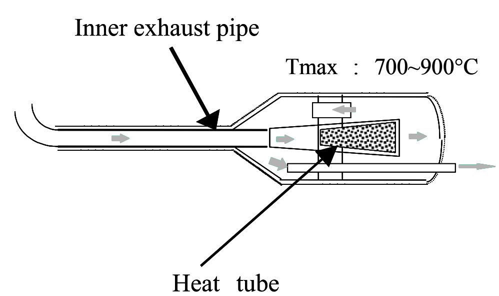

Figure 1. Schematic illustration of the motorcycle muffler

between the catalyst layer and the steel. Although the oxide scale of ferritic stainless steel such as Type436L (17Cr-1Mo-Ti steel), which is commonly used in muffler components, is mainly composed of Cr oxide, it also contains many Fe ions. Therefore, deterioration of the catalyst occurs due to diffusion of Fe ions from the oxide scale to the catalyst layer when Type436L is used without coating as a catalyst substrate. That is, oxidation resistance is required for materials used for the catalyst substrate to prevent deterioration of the catalyst. Al-containing stainless steels such as 20Cr-5Al steel have greater oxidation resistance than Type436L[2]. 18Cr-3Al stainless steel is one of the most common materials used for this catalyst substrate 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. In this work, the influences of Al and Si additions to high-purity ferritic stainless steel on oxidation resistance and formability were investigated and a new stainless steel having oxidation resistance equivalent to 18Cr-3Al and better formability than 18Cr-3Al were developed.

Alloy Design Concept

Al is a good alloying element to increase the oxidation resistance of steels. However, Al is an alloying element that also deteriorates the formability of steels. To develop steels with both excellent oxidation resistance and good formability, it is important that Al content is decreased to as little as possible while keeping excellent oxidation resistance. Therefore, the minimum content of Al in 18Cr steel with as excellent oxidation resistance as 18Cr-3Al steel was investigated.

In addition, to improve formability, the contents of C and N are decreased to as little as possible and Ti is added to stabilize them as titanium carbonitride. Therefore, chemical compositions based on high-purity 18Cr-Al-Ti steels are discussed in this development.

Experimental Procedure

Sample preparation

Chemical compositions of steels discussed below are shown in Table 1. These steels were melted in a vacuum induction furnace and cast to obtain 20 kg ingots. Each ingot was hot-rolled, cold-rolled, and annealed. Finally, steel sheets of 1.2 mm in thickness were prepared.

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

Oxidation Resistance

In this work, oxidation tests were performed in an actual exhaust gas atmosphere adjusted to 10% H_2O and 1% O_2 at temperatures between 500-1100ºC for 5 h. The reason that an actual exhaust gas atmosphere was used is that results obtained between in exhaust gas and in air might be different. Oxidation test samples were prepared by cutting and polishing the steel sheets.

After the oxidation tests, mass gains of oxidized samples were measured and their appearance was observed. In addition, some of the samples were observed in cross section by transmission electron microscopy (TEM) to investigate the oxide film structure. TEM samples were prepared by a focused ion beam (FIB) method.

Formability

The effects of Al and Si on formability were investigated. Tensile tests were performed in accordance with Japan Industrial Standard (JIS) to examine the formability of the steels. Tensile test specimens had gauge length of 50 mm and width of 12.5 mm at the gauge portion (JIS 13B type). In addition, to estimate the formability of welds of the steels, Erichsen tests were carried out. The samples were prepared by autogenous welding using a tungsten inert gas (TIG) welding process.

Experimental Results and Discussion

Oxidation resistance

Figure 2 shows the Al content dependence on the mass gain in the oxidation test in an exhaust gas atmosphere[3]. Above 800ºC, mass gains increase with increasing of Al content up to 1mass%. After that, they decrease remarkably with increasing of Al content until 2mass%. That is to say, the mass gain curves have peaks at 1mass% Al. In the case of Al content of 2mass% or more, the mass gains remain at a lower level. Al_2O_3 protective oxide films are considered to form on the metal surfaces. However, at 700ºC, the mass gain curve has a peak at 1.6mass% Al. This is considered to be due to Fe oxide, which is called red scale defect, forming on the metal surface. It is confirmed that the formation of red scale defect occurs only in an exhaust gas atmosphere at 700ºC and it does not occur in air at the same temperature[2]. Materials for mufflers with a catalyst are exposed to temperatures of approximately 700-900ºC. Therefore, it is important to suppress the formation of red scale defect at 700ºC.

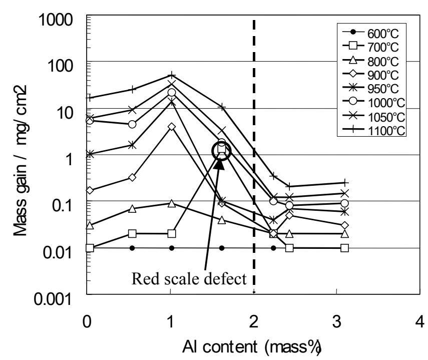

Figure 2. Al content dependence of mass gain after oxidation tests in an exhaust gas atmosphere for 5 h.

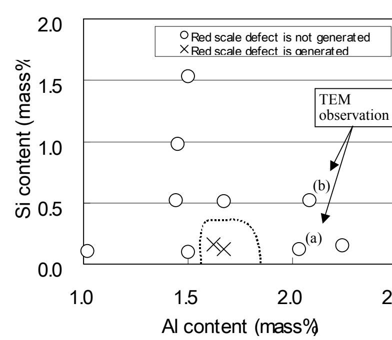

Figure 3. Effects of Al and Si on the formation of red scale defects in an oxidation test in an exhaust gas atmosphere at 700°C for 5h.

Figure 3 shows the effects of Al and Si on the formation of red scale defect at 700ºC for 5 h in an exhaust gas atmosphere[4]. The region of the formation of red scale defect, which is indicated by the dotted circle in Figure 3, is small around 1.6mass% Al. By adding more than 0.5mass% Si, red scale defect does not form.

To investigate the effect of Si on the suppression of the formation of red scale defect, two samples with different Si content (0.1mass% and 0.5mass%) and the same Al content (2mass%), which are indicated by the arrows in Figure 3, were examined by FE-TEM. The formation of red scale defect is not observed in either of them. However, thin Al_2O_3 films observed by TEM were different. Figure 4 shows TEM observation results of (a) 2Al-0.1Si steel and (b) 2Al-0.5Si steel. In the bright-field images (BFI) of both of them, thin oxide films are observed below white layers, which are W layers deposited on the surfaces to avoid the damage from FIB. However, the results of micro electron dispersive X-ray spectroscopy (μ-EDS) show that the compositions of the thin films of both samples are different. In Figure 4(a), Fe and Cr are obviously detected in addition to Al as metal elements in the oxide film. On the other hand, in Figure 4(b), Fe and Cr are hardly detected in the oxide film. That is to say, the oxide film on 2Al-0.1Si steel contains Cr and Fe as impurities and the oxide film on 2Al-0.5Si steel is essentially Al_2O_3 film.

Therefore, the 2Al-0.1Si steel is insufficient at 700ºC in an exhaust atmosphere and 2Al-0.5Si steel is required. In other words, to keep excellent oxidation resistance, more than 2mass% Al content and more than 0.5mass% Si content are required.

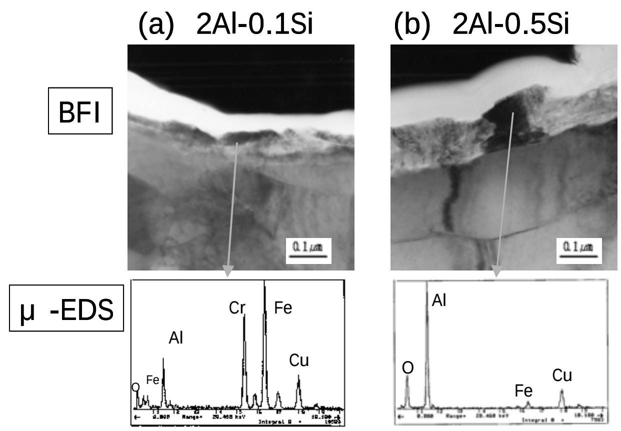

Figure 4. TEM observation results in a cross-sectional view (a) 2Al-0.1Si (b)2Al-0.5Si

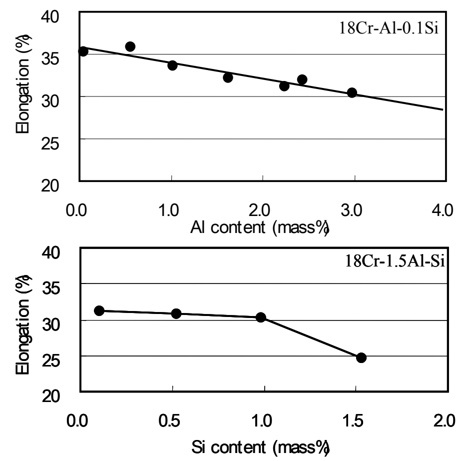

Figure 5. Effects of Al and Si on elongation

Formability

Figure 5 shows the effects of Al and Si on elongation of tensile tests. Elongation decreases almost linearly with increasing of Al content up to 3mass%. It is found that elongation does not vary with the addition of Si up to 1mass% and decreases sharply after that. Figure 6 shows the effects of Al and Si on the Erichsen value of TIG welds of the steels. The Erichsen value does not vary with the addition of Al up to 2mass% and that of Si content up to 0.5mass%.

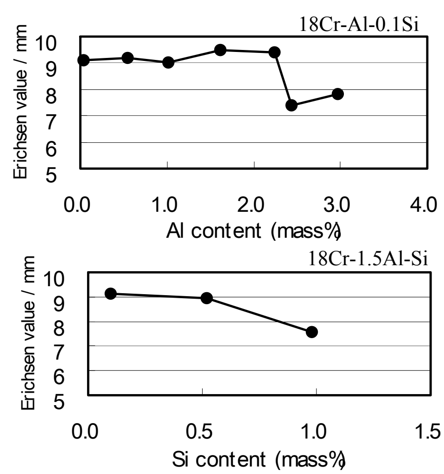

Figure 6. Effects of Al and Si on the Erichsen value of welds

After that, the Erichsen value decreases remarkably with increasing of Al and Si contents. The remarkable decrease is considered to be due to the ductility loss by Al addition.

Optimum compositions

From the evaluation of oxidation resistance, more than 2mass% Al content and more than 0.5mass% Si content are required. On the other hand, the evaluation of formability needs less than 2mass% Al content and less than 0.5mass% Si content. Therefore, it is concluded that 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.

Various Properties of Developed Steel

Table 2 shows an example of the chemical composition of the developed steel compared with that of conventional 18Cr-3Al steel. Both of these steels of 1 mm in thickness were examined to compare various properties. Oxidation tests were performed in an exhaust gas atmosphere in the same way as described above. However, samples with pasted catalyst were used. Also in the oxidation tests, samples were obtained by cyclic heating every 5 hours at 700ºC 10 times. Figure 7 shows the appearance of samples oxidized at 700ºC. The appearance of the developed steel does not change and deterioration of the catalyst was not observed, the same as with 18Cr-3Al steel. It indicated that the oxidation resistance of the developed steel is the same as that of 18Cr-3Al steel.

Table 2 Example of chemical compositions of the developed steel and the conventional 18Cr-3Al steel

Steels	Chemical compositions (mass%)								
	C	Si	Mn	P	S	Cr	Tí	N	Al
Developed Steel	0.0022	0.45	0.25	0.29	0.0007	18.1	0.17	0.0065	2.1
18Cr-3Al Steel	0.0080	0.25	0.22	0.32	<0.0003	18.2	0.16	0.0080	3.1

Figure 8 shows the elongation of the materials and the Erichsen value of the TIG welds of both steels. The elongation and Erichsen value of the developed steel is higher than those of the 18Cr-3Al steel. In particular, the elongation of the developed steel is as high as that of Type436L (17Cr-1Mo-Ti steel), which is commonly used for muffler materials.

It is confirmed that the developed steel has both excellent oxidation resistance and good formability.

Conclusion

The results obtained are as follows:

- Mass gains in oxidation tests are remarkably suppressed by adding more than 2 mass% Al due to the formation of an Al_2O_3 layer.
- Oxidation resistance is improved by adding more than 0.5mass% Si because the content of other elements such as Cr and Fe in the Al_2O_3 layers decreases with increasing Si content.
- Elongation increases with decreasing Al content. The Erichsen values of welds obviously decrease by adding more than 2.5mass% Al.

- Elongation does not vary with the addition of Si up to 1mass%.

From these results, it is concluded that 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 for catalyst substrate has excellent oxidation resistance equivalent to conventional 18Cr-3Al as well as formability better than 18Cr-3Al. It has in fact been used for mufflers in more than 100,000 motorcycles so far.

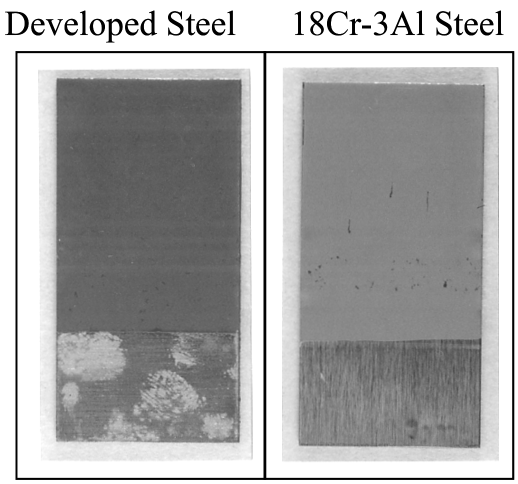

Figure 7. Appearance of steels with pasted catalyst after an oxidation test (700°C , 5h, 10times).

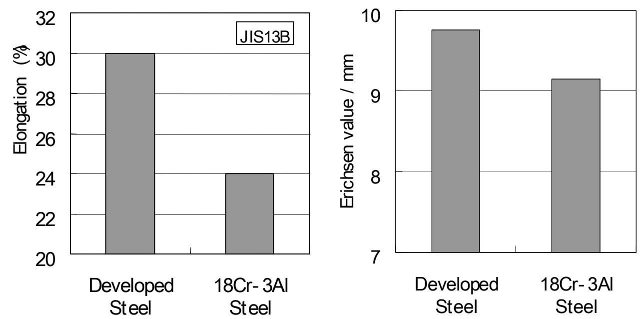

Figure 8. Formability of the developed steel in comparison with the conventional 18Cr-3Al steel.

References

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METAL PERFORMANCE REQUIREMENTS FOR AUTOMOTIVE FUEL CELLS

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Abstract

Automotive propulsion systems using proton exchange fuel cell technology poses unique material challenges. This poster will explain the requirements for adequate metal performance in fuel cells for automotive application.