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Development of High Heat-Resistant Ferritic Stainless Steel with High Formability, "RMH-1," for Automotive Exhaust Manifolds by Optimizing Mo Composition Design*



Atsushi Miyazaki
Senior Researcher,
Stainless Steel Lab.,
Technical Res. Labs.

Junichiro Hirasawa
Senior Researcher,
Stainless Steel Lab.,
Technical Res. Labs.

Osamu Furukimi
Dr. Eng.,
General Manager,
Stainless Steel Lab.,
Techinical Res. Labs.

Synopsis:

To develop a high heat-resistant stainless steel with high formability for automotive exhaust manifolds, the influences of Mo and Si contents on the formability, oxidation resistance, and high temperature strength of 14%Cr ferritic stainless steel were investigated. Mo addition increased oxidation resistance and high temperature strength remarkably. Si addition increased significantly oxidation resistance but had a little effect on high temperature strength. Based on these findings, a high heat-resistant Mo-added ferritic stainless steel with high formability, RMH-1 (14.5%Cr-0.3%Si-0.5%Nb-1.6%Mo), has been developed. The newly developed steel possesses not only the advantage of the existing high heat-resistant type but also that of high formability type stainless steels. Namely, RMH-1 possesses high temperature strength and fatigue properties equal to those of a conventional SUS444 steel, R434LN2 (19%Cr-0.3%Si-0.35%Nb-1.8%Mo), which is considered to be a high heat-resistant steel for automotive exhaust applications, combined with formability equal to that of the conventional R429EX (14.5%Cr-0.9%Si-0.45%Nb), which is used as a high formability steel in the same applications.

1 Introduction

With attention focused on global environmental problems, there has been strong demand in recent years for improvement in the purification ratio of automotive exhaust gas, accompanied by legal regulation in many nations. Examples of regulatory values for tail pipe exhaust gas emissions from gasoline-fueled automobiles which have been implemented or are now proposed include the Year 2000 regulations in Japan, Tier 1 and Tier 2 regulations in the United States, and Euro 3 and Euro 4 regulations in Europe.[1] In responding to this trend, improvement of exhaust gas purification characteristics immediately after the engine is started (cold start) is an extremely important task. This is because part of the heat of the exhaust gas is transfered to the exhaust manifold immediately after the engine is started, reducing the temperature of the exhaust gas, while at the same time, it is also difficult to proceed the purification reactions for the NO_X, HC and CO in the exhaust gas because the temperature inside the catalytic converter is low. As one solution to this problem, adoption of thinner wall material in the exhaust manifold reduces the heat capacity of this part, which makes it possible to flow the exhaust gas into the catalytic converter while still at a high temperature. This technique is already used commercially as a means of accelerating the purification reaction during cold starts.[2] Moreover, use of thinner wall material in the exhaust manifold also contributes to auto weight reduction. Because the manifold material should possess excellent heat resistance if this method is to be used, ferritic stainless steel is increasingly applied as a substitute for cast parts.[3] On the other hand, because the exhaust manifold is designed to fit into a restricted space in the auto body in many cases, high formability materials are also required. Kawasaki Steel previously developed two types of steel to meet these

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respective needs, a high heat-resistance type stainless steel, R434LN2 (SUS444), which gives priority to heat resistance, and a high formability stainless steel, R429EX, which gives priority to formability.[4,5] However, in recent years, even stricter requirements have been applied to heat resistance and formability in the exhaust manifold materials for many types of automobiles. Accompanying this trend, there was strong demand for the development of a stainless steel which possesses the advantages of both of the above-described steels. Concretely, this meant that the newly developed stainless steel should possess excellent heat resistance properties (high temperature strength, high temperature fatigue property, and thermal fatigue property) equal to those of R434LN2, together with the outstanding formability of R429EX.

Based on detailed research on the high temperature strength, oxidation resistance, and formability of ferritic stainless steels carried out at Kawasaki Steel, the company developed a new ferritic type stainless steel, RMH-1. The developed steel possesses both heat resistance properties (high temperature strength, high temperature fatigue property, thermal fatigue property) equivalent to those of R434LN2 at high temperatures in the range of 800°C to 950°C, and excellent formability equal to that of R429EX at room temperature. This article discusses the knowledge which was obtained through this development effort and summarizes the properties of RMH-1.

2 Sample Materials and Experimental Procedure

It has been reported that the thermal fatigue property and high temperature fatigue property, which are indexes of heat resistance, can be improved by increasing 0.2% proof stress (PS) at high temperature.[4,6,7] An element Mo addition is an effective means of increasing 0.2%PS at high temperatures, but also increases YS and TS at room temperature and reduces elongation. This means that deterioration in formability at room temperature would be a problem if Mo were simply added to R429EX with no other changes in the material design. As a means of compensating for this reduction in room temperature formability, the authors investigated the effects of Mo and Si on 0.2%PS at high temperatures, oxidation resistance, and formability using a 14%Cr steel as the basic composition, with special attention to a low Si design. The range of chemical compositions of the materials used in these experiments is shown in **Table 1**. Starting with small steel ingots, which were melted in a high frequency vacuum melting furnace, cold rolled steel sheets with a thickness of 2 mm were prepared by a process of hot rolling, annealing, cold rolling, and annealing, and were then subjected to the following tests (1)–(3). Solid round-bar test pieces were also prepared by forging and annealing, and were used in the thermal fatigue test in (4) below.

Table 1 Chemical compositions of steels used

(mass%)

C	Si	Mn	Cr	Mo	Nb	N
0.01	0.05–1.5	0.2	14	0–2	0.5	0.01

Cold rolled steel sheets (thickness, 2 mm) of the developed steel were manufactured at the company's works and evaluated by tests (1) through (3), together with the conventional high formability and high heat-resistance steels (R429EX, R434LN2) as comparison materials. The Schenck type high temperature fatigue property of these materials was also evaluated by the method described in (5).

(1) High Temperature Tensile Test

A high temperature tensile test was performed in accordance with JIS G 0567. After heating to the specified temperature, the specimens were held for 15 min, and 0.2%PS and TS were measured under strain rate conditions of 0.3%/min until 0.2%PS, followed by 8.3%/min until rupture.

(2) Oxidation Resistance Test

The configuration of the specimens was 2 mm (t) × 20 mm (w) × 30 mm (l). The materials used in this experiment were polished to #400, degreased, and given heat treatment for 200 h at 950°C. The relationship between the weight gain due to oxidation and the contents of Mo and Si was then investigated.

In the case of the cold rolled steel sheets manufactured in the works, degreasing was performed without polishing, and the weight gain due to oxidation was measured after heat treatment in air for 400 h at temperatures of 800°C, 900°C, 950°C, and 1 000°C.

(3) Room Temperature Tensile Test

Using JIS 13 B test pieces, YS, TS, El and the r-value were measured under a tensioning rate condition of 10 mm/min. The r-value was obtained after applying 15% strain. The average values of the measured results were obtained by Eq. (1), in which the directions 0°, 45°, and 90° relative to the rolling direction are expressed by X_L, X_D, and X_C, respectively.

$$X = (X_L + 2X_D + X_C) / 4 \cdots\cdots\cdots (1)$$

(4) Thermal Fatigue Test

The specimens were heated to 450°C under a no-load condition by using a load controller. Assuming α is the thermal expansion coefficient, the material expands by only α (450°C − room temperature) due to free thermal expansion up to this temperature, but no stress loading is applied. This condition was defined as the starting point at which strain loading was applied to the material. Strain was detected by using a differential transducer type extensometer with an extensometer gauge length of 15 mm. A heat cycle of 100°C − 800°C was applied, and the restraint ratio (η) shown below was controlled to 0.5 by an oil hydraulic servo method.

$$\eta = \Delta\varepsilon_t / \Delta\varepsilon_f = 0.5 \quad (2)$$
$$\Delta\varepsilon_t = \Delta\varepsilon_f - \Delta\varepsilon_c \quad (3)$$

Here,

η : Restraint ratio
$\Delta\varepsilon_t$: Total strain range
$\Delta\varepsilon_f$: Strain equivalent to free thermal expansion between 100°C − 800°C
$\Delta\varepsilon_c$: Apparent strain range detected by extensometer

(5) High Temperature Fatigue Test

Using a Schenck type high temperature plane bending fatigue test machine, *S-N* curves were prepared for 800°C and 900°C under conditions of $R = -1$ and a speed of rotation of 1 300 rpm. The value used for bending stress was obtained from dividing the bending moment measured at the point of Nf/2 cycles relative to the number of cycles to failure (Nf), by the cross sectional coefficient of the test piece.

3 Experimental Results and Discussion

3.1 Effect of Mo and Si on 0.2%PS at 900°C

Figure 1 shows the effect of the Mo and Si content on 0.2%PS at 900°C. A remarkable increase in 0.2%PS could be observed when Mo was added in the range of up to 1.5%, but beyond this content this showed a tendency to approach a constant value. Fujita et al.[8] investigated the effect of Mo addition on 0.2%PS at 950°C with 19%Cr-0.4%Nb steel and reported that the effect of Mo addition reaches saturation at 1.5% or above. Mo addition exhibited the same behavior in this experiment. In contrast, with Si addition, 0.2%PS remained virtually constant regardless of the amount added.

3.2 Effect of Mo and Si on Oxidation Resistance

Figure 2 shows the effect of the Mo content on weight gain due to oxidation in 14%Cr ferritic stainless steel.[9] Oxides comprising mainly Fe are shown in the figure by an asterisk (*) and indicate that abnormal oxidation is ocurring. It was found that Mo addition is remarkably effective in increasing oxidation resistance in 14%Cr steel at 950°C. **Figure 3** shows the effect of Si

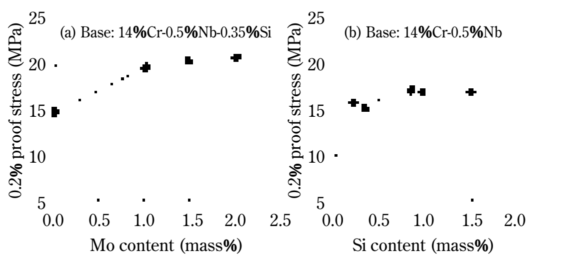

Fig. 1 Effect of (a) Mo and (b) Si contents on 0.2% proof stress at 900°C

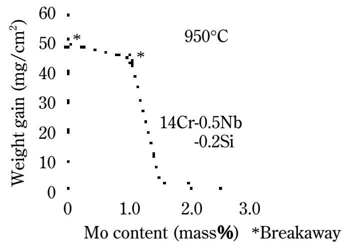

Fig. 2 Effect of Mo content on weight gain of 14%Cr-0.5%Nb-0.2%Si stainless steels by continuous heating at 950°C for 200 h in air

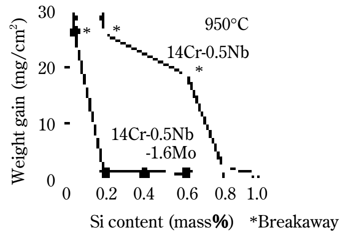

Fig. 3 Effect of Si content on weight gain of 14%Cr-0.5%Nb and 14%Cr-0.5%Nb-1.6%Mo stainless steels by continuous heating at 950°C for 200 h in air

addition on weight gain due to oxidation in non-Mo-added steel and 1.6%Mo-added steel. With Mo-free steel, an Si addition of 0.8% or more was necessary in order to suppress abnormal oxidation in the oxidation test at 950°C, but in contrast to this, it is clear that an Si addition of 0.2% or more is sufficient to achieve the same result with 1.6%Mo-added steel. In discussing the effects of Cr and Si, it is known that these elements continuously form an oxidation film consisting of Cr_2O_3, SiO_2, and other oxides, which possesses a strong protective property, when added in a certain amount or greater in a continuous oxidation test of ferritic type stainless steel, and the presence of this film enhances oxidation resistance.[10] However, according to reports of experimental results with 4%Si addition to 11%Cr steel[11] and 1%Si addition to 14%Cr steel,[12] Si addition was effective in suppressing abnormal oxidation in both cases, even though the formation of a distinct SiO_2 film could not be observed. The mechanism by which this improved oxidation resistance was obtained by Si addition is not completely clear. From the viewpoint of microstructure in metal, Fujikawa et al.[13] reported that if part of the microstructure undergoes the γ transformation in an oxidation test, abnormal oxidation occurs easily at that part, suggesting that the effect of Si on oxidation resistance is not due to the presence of a protective film, but rather, can be explained by enhanced stability of the ferrite microstructure. Likewise, considering the fact that continuous Si oxides and Mo oxides were not observed with the composition system used in the present experiments, even though continuous Cr oxides were noted, together with the fact that both Mo and Si are strong ferrite-forming elements, it can be considered that the addition of these elements to 14%Cr stainless steel enhances oxidation resistance by suppressing the formation of the γ phase at high temperature, in other words, by stabilizing the ferrite microstructure. Thus, the present experimental results, which showed that an Si addition of 0.8% or more is necessary with Mo-free steel, but only a small addition of 0.2%Si is sufficient with 1.6%Mo-added steel, are not interpreted according to the Si protective film theory, but rather, are interpreted as attributable to the fact that the ferrite phase can be stabilized by a smaller amount of Si in Mo-added steel. However, it is also necessary to consider a paper by Kobayashi et al.[14] in connection with Ti-added 18%Cr ferritic stainless steel, which stated that Mo affected the composition of the passivation film which formed at room temperature, and the passivation film then affected oxidation resistance. This suggests that a detailed study which includes such points as the fineness of the passivation film, etc. may also be necessary, in addition to the ferrite microstructure stabilization theory proposed by Fujikawa et al.

4 Concept of Composition Design of Developed Steel

From the results described earlier, it became clear that even though the Si content of R429EX (0.9%Si) contributes to improved oxidation resistance, it makes virtually no contribution to 0.2%PS at 900°C. Because Mo improves both oxidation resistance and 0.2%PS at high temperatures, Mo was positively utilized in the composition design of the newly developed steel, and the Si content was reduced. As a result, a new ferritic type stainless steel, RMH-1, with high heat resistance and high formability was developed, using 14.5%Cr-0.3%Si-1.6%Mo-0.5%Nb as the basic composition. The following chapter describes the features of the developed steel in comparison with the conventional steels used in the same applications.

5 Features of Developed Steel (RMH-1)

5.1 Chemical Composition and Mechanical Properties at Room Temperature

Table 2 shows the chemical compositions of the developed steel (RMH-1) and the conventional steels (R429EX, R434LN2). **Table 3** shows the room temperature mechanical properties of cold rolled sheets with a thickness of 2 mm. The YS, TS, El and *r*-values of RHM-1 are almost equal to those of R429EX, and in comparison with R434LN2, the strength of RMH-1 is lower and its elongation and *r*-value are higher.

Table 2 Chemical compositions of RMH-1, R429EX, and R434LN2

(mass**%**)

	C	Si	Mn	Cr	Mo	Nb
RMH-1	0.004	0.34	0.18	14.5	1.6	0.46
R429EX	0.008	0.86	0.37	14.6	–	0.44
R434LN2	0.005	0.28	0.16	18.7	1.8	0.34

Table 3 Mechanical properties of RMH-1, R429EX and R434LN2

	Direction	YS (MPa)	TS (MPa)	El (**%**)	*r*
RMH-1	L	307	474	37	1.6
	D	330	500	31	1.1
	C	320	478	36	2.1
	Average	322	488	34	1.5
R429EX	L	308	483	36	1.5
	D	337	511	32	1.1
	C	330	495	34	2.0
	Average	328	500	33	1.4
R434LN2	L	366	518	33	1.2
	D	400	543	29	0.9
	C	390	528	32	1.6
	Average	389	533	31	1.2

Sheet thickness: 2.0 mm

Table 4 Mechanical properties of ERW pipes according to JIS 11

	YS (MPa)	TS (MPa)	El (**%**)
RMH-1	487	512	51
R429EX	491	531	49

Table 4 shows the mechanical properties of electric resistance welded tubes with a diameter of 48.6 mm and thickness of 2.0 mm. The YS, TS, and El of the ERW tube of RMH-1 exhibited values almost equal to those of R429EX.

5.2 High Temperature Properties

Figure 4 shows 0.2%PS and TS at 800°C and 900°C. RMH-1 showed higher high-temperature strength than R429EX and values almost equal to those of R434LN2.

Figure 5 shows weight gain due to oxidation after heating treatment in air for 400 h at temperatures of

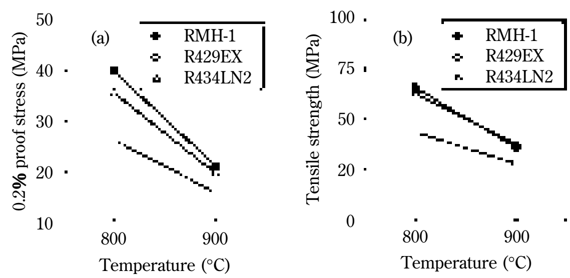

Fig. 4 High-temperature strength; (a) 0.2%proof stress (b) tensile strength

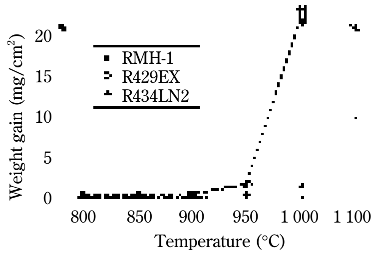

Fig. 5 Oxidation test results of RMH-1, R429EX, and R434LN2 between 800°C and 1 000°C for 400 h in air

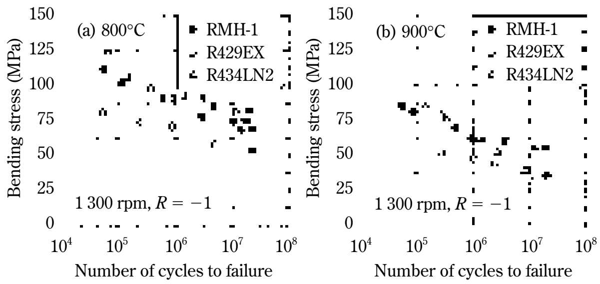

Fig. 6 *S-N* curves of RMH-1, R429EX, and R434LN2; (a) 800°C, (b) 900°C

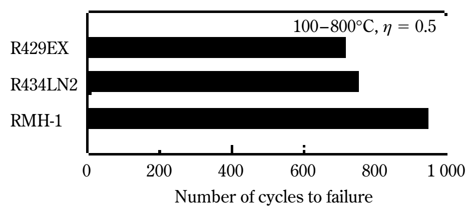

Fig. 7 Comparison of thermal fatigue life between RMH-1 and conventional stainless steels

800°C, 850°C, 900°C, 950°C, and 1 000°C. RMH-1 showed satisfactory oxidation resistance, substantially equal to that of R429EX.

Figure 6 shows *S-N* curves for 800°C and 900°C. The 10^7 fatigue limit of RMH-1 was higher than that of R429EX and showed a value substantially equal to that of R434LN2.

Figure 7 shows the thermal fatigue test results. RMH-1 exhibited a longer fatigue life than either R429EX or R434LN2.

6 Conclusions

With stricter regulation of automotive exhaust gas in recent years, the service environment for stainless steel is becoming increasingly severe. For this reason, there had been strong demand for the development of a stainless steel which possesses both high heat resistance and excellent formability, particularly for application in high temperature environments represented by the exhaust manifold, front pipe, catalytic converter case, and similar parts. In order to meet these requirements, Kawasaki Steel carried out detailed research on the effect of Mo and Si on heat resistance and formability, and succeeded in developing a new ferritic stainless steel (RMH-1) by adopting a composition design that makes the maximum use of the effectiveness of Mo. The new steel possesses excellent heat resistance properties (high temperature strength, high temperature fatigue property, and thermal fatigue property) almost equal to those of R434LN2 (SUS444), which is the conventional high heat-resistance material for exhaust manifolds, and outstanding formability, almost equal to that heat-resistance material for exhaust manifolds, and outstanding formability, almost equal to that of R429EX, which is a high formability material for exhaust manifolds. In the future, a continuing trend toward stricter regulation of exhaust gas is likely in virtually all countries worldwide. Because RMH-1 with high heat-resistance and high formability can meet the requirements of these stricter regulations, further increases in the adoption of this material are foreseen, and expected to contribute to a cleaner environment.

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