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Ferritic Stainless Steel for Automotive Exhaust Systems —High Heat-Resistant Ferritic Stainless Steel with High Formability for Automotive Exhaust Manifolds: "JFE-MH1"—†

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Abstract:

The effects of Mo and Si on formability, high temperature strength, and oxidation resistance of the 15%Cr ferritic stainless steel were investigated in order to develop a high heat-resistant, high formability stainless steel suitable for automotive exhaust manifolds. The Mo addition displays a remarkable effect in improving oxidation resistance and high temperature strength. The Si addition is effective in improving oxidation resistance, but was found to have virtually no effect in improving high temperature strength. Based on these findings, a new Mo-added ferritic stainless steel with excellent heat resistance and formability was developed. The new steel, JFE-MH1 (15%Cr-0.3%Si-0.5%Nb-1.6%Mo), possesses the combined advantages of two existing steels (high formability type and high heat-resistant type). Specifically, JFE-MH1 steel sheets and ERW tubes show formability equal to the values of the existing high formability stainless steel, JFE429EX (15%Cr-0.9%Si-0.5%Nb), and high temperature strength, high temperature fatigue properties, and thermal fatigue properties superior to those of the existing high heat-resistant stainless steel JFE434LN2 (SUS444: 19%Cr-0.3%Si-0.3%Nb-1.9%Mo).

1. Introduction

In recent years, with attention focused on global environmental problems, improvement in automotive exhaust gas purification ratios has been strongly required under legal regulations in many countries. Examples of exhaust gas regulations for gasoline-powered passenger cars which have already been implemented or are proposed include the Year 2000 and 2005 regulations in Japan, Euro 3 and 4 regulations in Europe, Tier 1 and 2 federal regulations in the U.S., and LEV 1 and 2 regulations in California, which are stricter than the federal government regulations.[1,2] In responding to these trends, improved exhaust gas purification characteristics immediately after starting the engine (cold start) becomes an extremely important problem.[2] Under these conditions, the purification reactions for NOx, HC, and CO in the exhaust gas are difficult to achieve because part of the heat of the exhaust gas is lost to the exhaust manifold during a cold start, lowering the temperature of the exhaust gas, while at the same time, the temperature of the catalytic converter is also low. To accelerate the purification reactions, the technique of introducing the exhaust gas into the catalytic converter while maintaining a high exhaust gas temperature by reducing the thickness of the exhaust manifold material so as to decrease its thermal capacity is already in practical use.[3] Moreover, reduction of the exhaust manifold material thickness also contributes to weight reduction. Because high heat resistance is required to materials when using this method, application of ferritic stainless steel as a substitute for cast iron is increasing.[4] On the other hand, in many cases, the exhaust manifold is designed with a

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complex shape to fit the limited auto body space, requiring high formability. JFE Steel had previously developed JFE434LN2 (SUS444) as a stainless steel with priority placed on heat resistance and JFE429EX as a stainless steel with high formability.[5,6] Recently, however, the heat resistance and formability requirements placed on exhaust manifold materials in many types of automobiles have become more severe, and there had been strong demand for the development of a stainless steel which combines the advantages of these two steels. Concretely, this meant the development of a ferritic stainless steel which possesses high heat resistance (high temperature strength, high temperature fatigue properties, and thermal fatigue properties) equal or superior to that of JFE434LN2 (SUS444), together with high formability equal to that of JFE429EX.

JFE Steel therefore carried out detailed research on the high temperature strength, oxidation resistance, and formability of ferritic stainless steel, and as a result, developed a new ferritic stainless steel, “JFE-MH1,” with heat resistance (high temperature strength, high temperature fatigue properties, and thermal fatigue properties) superior to that of JFE434LN2 at high temperatures from 800°C to 950°C, combined with excellent formability equivalent to that of JFE429EX at room temperature. This paper describes the knowledge obtained in this development and introduces the features of JFE-MH1.

2. Samples and Experimental Procedure

It has been reported that increasing 0.2% proof stress (PS) at high temperatures is useful for improving thermal fatigue properties and high temperature fatigue properties, which are indexes of heat resistance.[5,7,8] Although addition of Mo is effective in improving 0.2% PS at high temperatures, at the same time, Mo increases room temperature yield strength (YS) and tensile strength (TS) and reduces elongation. This means that simply adding Mo to JFE429EX (15%Cr-0.9%Si-0.5%Nb) would result in the problem of reduced formability at room temperature. To compensate for this reduction in room temperature formability, a low-Si design was studied, and the effects of Mo and Si on 0.2% PS at high temperatures, oxidation resistance, and formability at room temperature were investigated using a 15%Cr steel as the basic composition. **Table 1** shows the chemical composition range of the steels in these experiments. Using small steel ingots melted in a high frequency vacuum melting furnace, cold-rolled and annealed steel strips (thickness: 2 mm) were prepared by a process of hot rolling, annealing, cold rolling, and annealing and used in the tests described in the following sections (1) through (3). In addition, solid round bar test pieces were prepared by forging and annealing and used in the thermal fatigue test in section (4).

Table 1 Chemical composition of steel used

(mass%)

C	Si	Mn	Cr	Mo	Nb	N
0.01	0.05–1.5	0.2	15	0–2	0.5	0.01

Next, cold-rolled and annealed strips of the developed steel produced in the works were evaluated as described in sections (1) through (3), together with the existing steels (JFE429EX, JFE434LN2) as comparison steels. High temperature fatigue properties were also evaluated as described in section (5).

(1) High Temperature Tensile Test

As stipulated in JIS G 0567, after reaching the specified temperature and holding for 15 min, 0.2% PS and TS were measured under strain rate conditions of 0.3%/min up to 0.2% PS, followed by 8.3%/min until fracture.

(2) Oxidation Resistance Test

The test piece was 2 mm thick, 20 mm wide, and 30 mm long. The cold-rolled and annealed steel strips prepared in the laboratory were polished to #400 and degreased, then subjected to a heat treatment at 950°C for 200 h to investigate the relationship between the contents of Mo and Si and weight gain due to oxidation. The cold-rolled and annealed steel strips produced in the works were prepared by degreasing without polishing, and weight gain due to oxidation after the heat treatment in the atmosphere for 400 h at temperatures of 800°C, 850°C, 900°C, 950°C, and 1 000°C was measured.

(3) Room Temperature Tensile Test

Using JIS No. 13B test pieces, YS, TS, El, and r-values were measured at the tensile speed of 10 mm/min. The r-value was obtained after applying 15% strain. The average of these values was calculated by Eq. (1) from the values when properties in the 0°, 45°, and 90° directions relative to the rolling direction are indicated by X_L, X_D, and X_C.

$$\text{Average of } X = \frac{X_L + 2X_D + X_C}{4} \quad \cdots\cdots\cdots\cdots (1)$$

(4) Thermal Fatigue Properties

Using an hydraulic servo-type thermal fatigue test machine, the specimen was heated to 450°C under no-load control. When α is the thermal expansion coefficient, the material elongates only by $\alpha \cdot \{450°\text{C} - (\text{room temperature})\}$ due to free thermal expansion up to this temperature. However, a load was not applied. This condition was used as the starting point for stress and strain in the material.

From this point, an out of phase-type strain control was performed. In apparent strain detection, a heat cycle of 100–800°C was applied so as to obtain a restraint ratio (η) of 0.5, as defined by Eq. (2), using a differential transformer type extensometer with an extensometer gauge lenfth of 15 mm.

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

$$\Delta\varepsilon_t = \Delta\varepsilon_f - \Delta\varepsilon_c \quad (3)$$

where,

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

(5) High Temperature Fatigue Test

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

3. Results and Discussion

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

Figure 1 shows the effects of the Mo and Si contents on 0.2% PS at 900°C. When Mo is added in the range up to 1.5%, a significant increase in 0.2% PS could be observed, but with addition above this level, improvement tended to level off. Fujita et al.[9] investigated the effect of Mo on 0.2% PS at 950°C for the 19%Cr-0.4%Nb steel and reported that the effect levels off with the addition of more than 1.5%. The Mo addition showed a similar behavior in the present experiment. On the other hand, in the case of Si, 0.2% PS was substantially constant independently of the amount of addition.

3.2 Effects of Mo and Si on Oxidation Resistance

Figure 2 shows the effect of Mo on weight gain due to oxidation in ferritic stainless steels.[10] Oxides comprising mainly Fe, in other words, the case were abnormal oxidation has occurred, are shown by the * mark in the figure. It can be understood that the addition of Mo is significantly effective in improving the oxidation resistance of the 15%Cr steel at 950°C.

Figure 3 shows the effect of Si on weight gain due to oxidation for the 15%Cr steels without Mo addition and with 1.6% Mo addition.[10] The results indicated that, in the steel without Mo addition, Si addition of 0.8% or more is necessary to prevent breakaway in the oxidation test at 950°C, but in contrast, for the 1.6% Mo-added steel, Si addition of 0.2% or more is sufficient. In explaining the effects of Cr and Si in the continuous oxidation test of ferritic stainless steels, when certain amounts of these elements are added, it has been proposed that Cr and Si improve oxidation resistance by forming a continuous oxidation film of Cr_2O_3 and SiO_2, etc., which has an excellent protective property.[11] How-

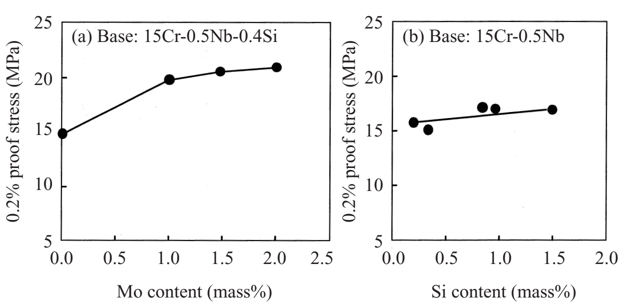

Fig. 1 Effects of (a) Mo and (b) Si contents on 0.2% proof stress at 900°C

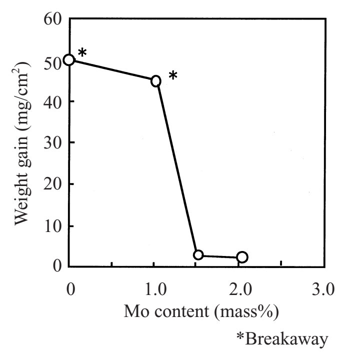

Fig. 2 Effect of Mo content on weight gain of 15%Cr-0.2%Si-0.5%Nb stainless steels by continuous heating at 950°C for 200 h in air

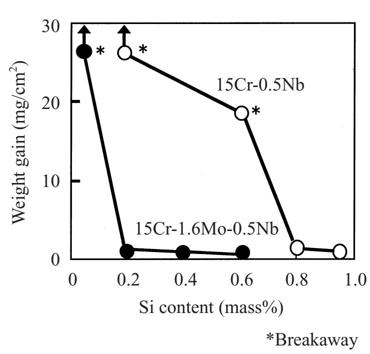

Fig. 3 Effect of Si content on weight gain by continuous heating at 950°C for 200 h in air

ever, in experiments when 4% Si was added to the 11% Cr steel[12)] and when 1% Si was added to the 14%Cr steel,[13)] in both cases it was reported that Si is effective in preventing abnormal oxidation even though formation of a distinct SiO_2 film could not be observed. Thus, the mechanism by which Si improves oxidation resistance is not necessarily clear. On the other hand, from the viewpoint of microstructure in metal, Fujikawa et al.[14)] reported that, when part of the microstructure in the oxidation test has undergone the γ transformation, abnormal oxidation tends to occur easily from that part, and, therefore, the effect of Si on oxidation resistance can be explained by stability of the ferrite structure, and not by the existence of protective film. Similarly, with the composition system used in these experiments, although continuous Cr oxides were observed, considering the facts that continuous Si oxides and Mo oxides were not observed, and both Mo and Si are powerful ferrite-forming elements, it can also be thought that the addition of these elements to the 15%Cr steel improves oxidation resistance by suppressing formation of the γ phase at high temperature and stabilizing the ferrite structure. In other words, the experimental results in the oxidation test at 950°C showing that the addition of 0.8% Si or more is necessary to prevent abnormal oxidation in steel without Mo addition, but only a small addition of 0.2% Si is sufficient for the 1.6% Mo-added steel, can be explained by the interpretation that the ferrite phase is stabilized with a smaller amount of Si in the 1.6% Mo-added steel, and not by an interpretation based on the Si protective film theory. However, considering a report by Kobayashi et al.[15)] that Mo influences the composition of the passivation film which forms at room temperature for the Ti-added 18%Cr ferritic stainless steel, and this passivation film influences subsequent oxidation resistance, a detailed study including the density of the passivation film and other viewpoints may be necessary, in addition to the ferrite structure stabilization theory proposed by Fujikawa et al.

4. Concept of Composition Design of Developed Steel

The results described above revealed that, although Si in JFE429EX (0.9%Si) contributes to the improvement of oxidation resistance, it makes virtually no contribution to 0.2% PS at 900°C. Accordingly, in the composition design of the developed steel, Mo was actively used, as it improves both oxidation resistance and 0.2% PS at high temperatures, while the Si content was reduced, and a high heat-resistant, high formability ferritic stainless steel, JFE-MH1, was developed using 15%Cr-0.3%Si-1.6%Mo-0.5%Nb as the basic composition.

The next chapter introduces the properties of the developed steel in comparison with the conventional steels.

5. Properties of Developed Steel, "JFE-MH1"

5.1 Chemical Composition and Room Temperature Properties

Table 2 shows the chemical compositions of the developed steel, "JFE-MH1," and the existing steels, "JFE429EX" and "JFE434LN2." **Table 3** shows the room temperature mechanical properties of cold-rolled and annealed sheets (thickness: 2 mm) of the same steels. JFE-MH1 shows YS, TS, El, and *r*-values similar to those of JFE429EX, and has lower strength and higher elongation and *r*-values than JFE434LN2.

Table 4 shows the mechanical properties of ERW steel pipes (diameter: 42.7 mm, thickness: 1.5 mm). The JFE-MH1 ERW steel pipes display YS, TS, and El values similar to those of JFE429EX. **Photo 1** shows the appearance of an ERW pipe of JFE-MH1 after 3-point bending at the bending radius of 50 mm and the bending angle of 90°. The arrow in the photo indicates the position of the maximum thickness reduction ratio. **Figure 4** shows the longitudinal thickness reduction ratio with this position as the center (0) point. JFE-MH1 demonstrated excellent formability equivalent to that of JFE429EX, which is a high formability stainless steel.

Table 2 Chemical composition of JFE-MH1, JFE429EX, and JFE434N2

(mass%)

	C	Si	Mn	Cr	Mo	Nb
JFE-MH1	0.004	0.34	0.18	14.5	1.6	0.46
JFE429EX	0.008	0.86	0.37	14.6	–	0.44
JFE434LN2	0.005	0.28	0.16	18.7	1.8	0.34

Table 3 Mechanical properties of JFE-MH1, JFE429EX, and JFE434LN2

(mass%)

	Direction	YS(MPa)	TS(MPa)	El(%)	*r*
JFE-MH1	L	307	474	37	1.6
	D	330	500	31	1.1
	C	320	478	36	2.1
	Average	322	488	34	1.5
JFE429EX	L	308	483	36	1.5
	D	337	511	32	1.1
	C	330	495	34	2.0
	Average	328	500	33	1.4
JFE434LN2	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 (1.5 mm*t* × 42.7 mmø) according to JIS 11

	YS(MPa)	TS(MPa)	El(%)
JFE-MH1	496	528	51
JFE429EX	516	534	49

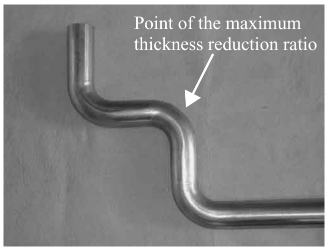

Photo 1 Appearance of ERW pipe of JFE-MH1 after 50 mm*R*-90° bending at three positions

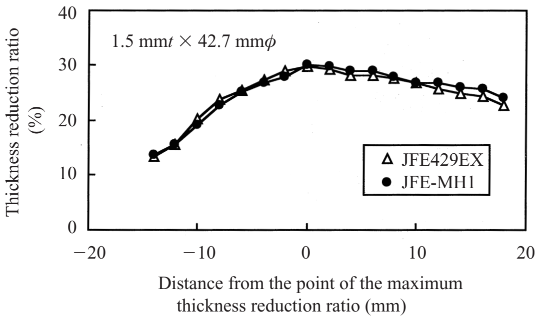

Fig. 4 Comparison of thickness reduction ratio after 90° bending between JFE-MH1 and JFE429EX stainless steel ERW pipes

5.2 High Temperature Properties

Figure 5 shows 0.2% PS and TS at 800°C and 900°C. The 0.2% PS of JFE-MH1 is superior to that of JFE434LN2, which is a high heat-resistant stainless steel.

Figure 6 presents a comparison of weight gain due to oxidation after heat treatment in the atmosphere for 400 h at 800°C, 850°C, 900°C, 950°C, and 1 000°C. JFE-MH1 displayed satisfactory oxidation resistance equivalent to that of JFE429EX.

The *S*-*N* curves at 800°C and 900°C obtained by the high temperature bending fatigue test and the fatigue strengths at 10^7 cycles obtained from these *S*-*N* curves are presented in **Fig. 7** and **Fig. 8**, respectively. The high temperature fatigue properties of JFE-MH1 are excellent, being equal or superior to those of the high heat-resistant stainless steel, JFE434LN2. In particular, at 900°C, the fatigue strength at 10^7 cycles of JFE-MH1 was approximately 50% higher than that of the high formability stainless steel, JFE429EX and was equal to the fatigue strength of JFE429EX at 800°C.

Figure 9 shows the results of the thermal fatigue test. JFE-MH1 displayed a longer thermal fatigue life than JFE429EX and JFE434LN2.

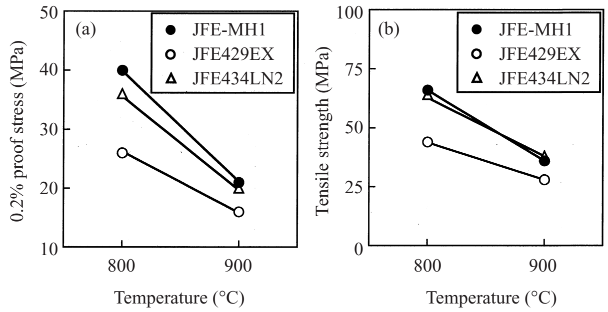

Fig. 5 Strengths at elevated temperatures; (a) 0.2% proof stress, (b) tensile strength

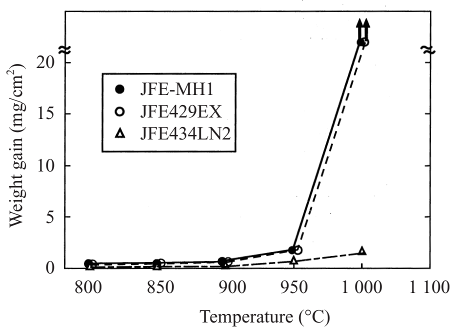

Fig. 6 Oxidation test results at 800°C to 1 000°C for 400 h in air

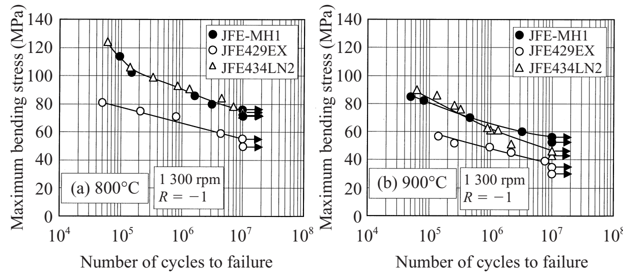

Fig. 7 *S*-*N* curves obtained by bending fatigue tests at (a) 800°C and (b) 900°C

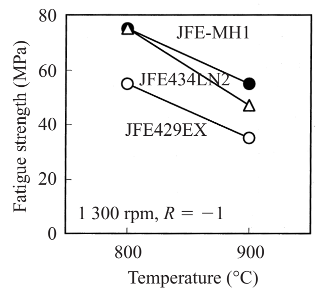

Fig. 8 Relation between 10^7 cycles fatigue strength vs. temperature

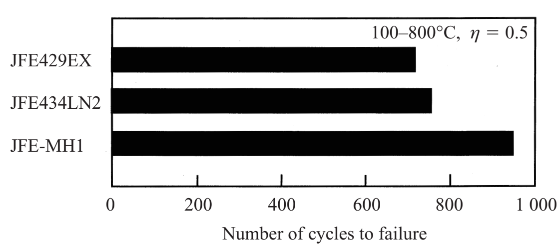

Fig. 9 Comparison of thermal fatigue life between JFE-MH1 and conventional stainless steels

6. Conclusion

With stronger regulations on automotive exhaust gas in recent years, the service environment for exhaust system parts is becoming increasingly severe. Therefore, development of stainless steels with high heat resistance and excellent formability for application in high temperature environments, in particular, as represented by the exhaust manifold, front pipe, and catalytic converter case, has been strongly required. To meet these requirements, JFE Steel succeeded in developing a new ferritic stainless steel, “JFE-MH1,” which possesses both high heat resistance (high temperature strength, high temperature fatigue properties, and thermal fatigue properties) equal or superior to those of SUS444, “JFE434LN2,” which is a representative conventional high heat-resistant stainless steel, and high formability equal to that of JFE429EX, which is a high formability stainless steel. In the future as well, a trend toward strengthening of exhaust gas regulations is foreseen in countries around the world. Because high heat resistance, high formability stainless steel JFE-MH1 is capable of satisfying these stronger regulations, this new product is expected to enjoy the expansion of use, contributing to a cleaner environment.

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