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


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Synopsis:

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1 I d c

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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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, curves were prepared for 800°C and 900°C under conditions of = −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 E e e a Re a d D c

3.1 Effec f M a d S 0.2%PS a 900 C

F e 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 Effec f M a d S O da Re a ce

F e 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. **F e 3** shows the effect of Si

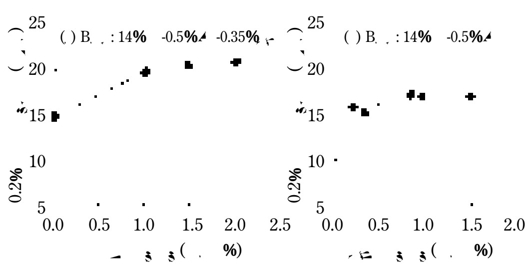

Fig. 1 Effect of (a) Mo and (b) Si contents on 0.2% proof stress at 900°C

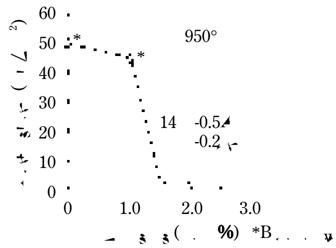

Fig. 2 Effect of Mo content on weight gain of 14%Cr-0.5%Nb-0.2%Si stainless steels by continuous heating at 950°C for 200 h in air

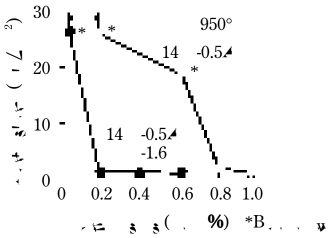

Fig. 3 Effect of Si content on weight gain of 14%Cr-0.5%Nb and 14%Cr-0.5%Nb-1.6%Mo stainless steels by continuous heating at 950°C for 200 h in air

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

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

F e 6 shows 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.

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

6 C c

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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