Technical Report

Development of NSSC™ EM-T Stainless Steel for Automotive Exhaust Systems

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Abstract

Ferritic stainless steel is widely used for the exhaust manifolds of automobiles. In recent years, vehicle emission control and fuel economy regulations have become increasingly strict. For this reason, there is an increasing demand for high heat resistance and thin wall materials for exhaust manifolds, as well as demand for materials with high heat resistance that is higher than the heat resistance temperature of the Type 444 series, which is currently the highest grade steel. We conducted various studies aiming at a heat-resistant temperature 70°C higher than the Type 444 series, and identified the appropriate addition amounts of W, Mo, Nb and Cu, leading to the development of the new steel grade NSSC EM-T (17Cr-2Mo-1.5Cu-1.3W-0.5Nb).

1. Introduction

In appreciation of its excellent high-temperature properties, stainless steel is widely used for the heat-resistant parts of various plant equipment, automobiles and combustion facilities. Especially for applications in which heating and cooling are repeated, ferritic stainless steel is more suitable than austenitic stainless steel because of its low thermal expansion coefficient and consequent superior thermal fatigue characteristics and good adhesion of the oxide scale.

Ferritic stainless steel is widely used for the exhaust manifolds of automobile engines. Soon after their material was changed from cast iron to stainless steel sheets and pipes, JIS SUS430J1L (19Cr-0.5Cu-0.4Nb) was mainly used for this application, but thereafter, stainless-steel makers developed a wide variety of new steel grades for the manifolds. As examples of such developments, **Fig. 1** shows the product lineup of Nippon Steel Stainless Steel Corporation for application to exhaust manifolds. The developed steel grades can be grouped as follows: the type 429 series (NSSC FH-Z and NSSC HR-1) for use up to 830°C with Nb addition to a basic alloy composition of highly formable 14 mass%Cr (hereinafter "mass%" in alloy composition is omitted); NSSC HR-2 and NSSC 429NF, in which the amounts of Cr and Nb are lower than in the type 429 series; the type 444 series (NSSC 190EM, NSSC 444M1, NSSC EM-3 and NSSC EM-2) for use up to 880°C with Nb and Mo addition to a basic alloy composition of 18Cr; and the type 448 series (NSSC 448EM and NSSC EM-C) for use up to 850°C having a basic alloy composition of the type 444 but containing less Mo and, instead, more Cu for higher strength.[1–5)]

In the meantime, in accordance with the latest efforts to deter global warming, the regulations on automobile exhaust gas and fuel

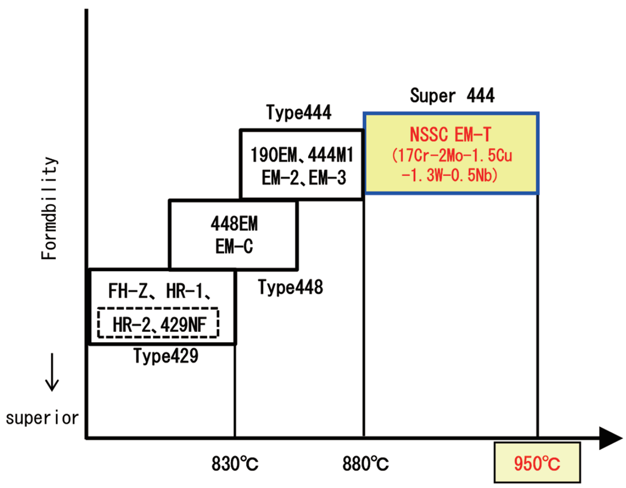

Fig. 1 Heat resistance of different types of stainless steel

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consumption are becoming increasingly strict. For example, of the fuel consumption regulations in Japan, the New Long-term Regulation set forth in 2005 and the Post-New Long-term Regulation in 2009 stipulated a combined starting method for the fuel consumption test of engines, that is, engines were tested in two modes, after warming up (hot start) and without it (cold start). However, according to all the relevant regulations instituted in 2018 and thereafter, cold start has been defined as the standard.[6] This means that it is important now to quickly warm up the engines so that the converter catalyst is heated up to its working temperature within a short time, and to this end, the wall thickness of exhaust manifolds has been decreased. To reduce the emission of NOx, HC, CO, etc. and improve fuel efficiency, car builders are studying combustion at a stoichiometric air-fuel ratio ($\lambda=1$), lean burn and weight reduction through the downsizing of engines. All these require higher heat resistance and lighter gauges of the manifold materials. Currently, automobile manufacturers select materials that are suitable for the exhaust gas temperature of their engines, but some of them are said to further raise the exhaust gas temperature, and request a heat resistance temperature as high as 950°C, which is beyond the ability of the type 444 series, presently the highest grade of ferritic stainless steel. In this context, development of a new grade of ferritic stainless steel for exhaust manifold use superior to the type 444 in heat resistance has been anticipated.

Facing the requirements for higher heat resistance of the material, we studied how to create a new steel grade that would exhibit thermal fatigue characteristics, high-temperature strength and oxidation resistance at high temperature superior to those of the type 444 and have equal workability and good low-temperature toughness for the ease of commercial production. The target of withstanding temperature was set at 950°C, higher by 70°C than 880°C of the type 444. This paper presents the studies for the development of NSSC EM-T (17Cr-2Mo-1.5Cu-1.3W-0.5Nb).

2. Target Properties

Table 1 shows the target properties aimed at in the development. Thermal fatigue properties were regarded as the most important issue, and the target figures were set specifically as follows: ① the thermal fatigue life of the developed NSSC EM-T at 200 to 950°C would have to be equal to or better than that of the type 444 series at 200 to 880°C; ② as for high temperature strength, 0.2% proof stress to be equal to or higher than that of the type 444 in all the temperature range of use; ③ regarding high temperature oxidation, no abnormal oxidation or flaking of oxide scale would be allowed up to 950°C; ④ workability would have to be equal to that of the type 444; and ⑤ the Charpy impact value of hot rolled and annealed sheets at 0°C would have to be 20 J/cm^2 or more.

Table 1 Target properties

Items	Target characteristics
① Thermal fatigue life	Number of cycles to failure at 950°C (Type444 + 70°C)
② High temperature strength	0.2% yield stress higher than that of type 444 in all temperature range of use
③ High-temperature oxidation	No abnormal oxidation or scale flaking at 950°C
④ Workability	Workability equal to that of type 444 (Total elongation, r value)
⑤ Low temperature toughness	Charpy impact value of hot rolled and annealed sheets at 0°C is 20 J/cm^2 or more

3. Alloy Design Concept

To achieve the target thermal fatigue life, the most important issue, it is effective to increase steel strength in the entire temperature range of use. **Figure 2** shows a schematic stress-strain diagram of the thermal fatigue test. Elastic and plastic stresses are imposed during a heat cycle, and thermal fatigue failure occurs as a result of repeating the A→B→C→D→E cycle in the diagram. Here, the range of inelastic strain (hereinafter abbreviated as $\Delta\varepsilon_p$) is defined as the strain difference between two points of a cycle at which the stress is 0; this is an important factor that determines thermal fatigue life. There is a good linear relationship between the logarithm of the number of cycles to failure at the test and that of $\Delta\varepsilon_p$,[7] and thermal fatigue properties become better with smaller $\Delta\varepsilon_p$. Based on this and in order to achieve the target thermal fatigue life, we looked for measures to make the $\Delta\varepsilon_p$ of the developed steel at 200 to 950°C smaller than that of the type 444 at 200 to 880°C. We also examined the effectiveness of simultaneous use of the two methods applied to the types 444[5] and 448[2, 3]: in the development of the type 444, the solid solution hardening with Mo and Nb was mainly used to increase the strength at high temperature and suppress the bulging and buckling of steel sheets during heating, and in the development of the type 448, the precipitation hardening (dynamic precipitation) with Cu and Nb was mainly used to increase the strength at medium to low temperature and suppress the necking of steel sheets during cooling. The dotted curves in red in Fig. 2 show the concept of how to decrease $\Delta\varepsilon_p$. In the present development, $\Delta\varepsilon_p$ was decreased by increasing strength in the entire temperature range of use from room temperature to high temperature.

Although it is considered possible to increase steel strength to a reasonable extent by adding strengthening elements in large quantities, it is not advantageous in terms of the material costs and workability of the product. Moreover, toughness is lowered with higher alloy contents, and as a consequence, additional processing may become necessary in commercial production, which means higher manufacturing costs. It is therefore important to limit the addition amounts of strengthening elements to the minimum required. Ac-

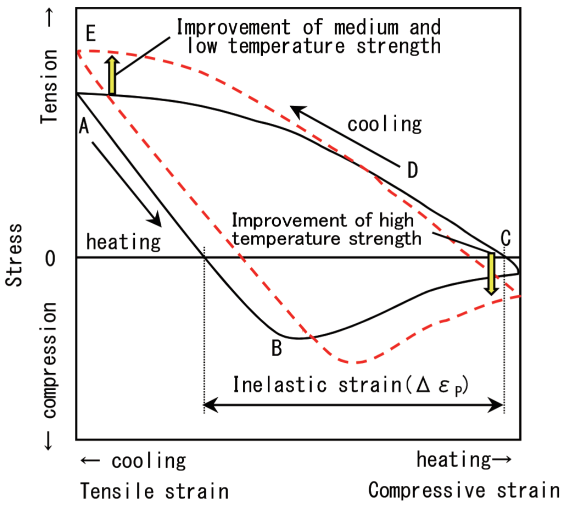

Fig. 2 Schematic diagram of stress-strain curve in thermal fatigue test

cordingly, to define their adequate addition amounts required for increasing steel strength at room temperature to high temperature, the effects of such elements on the alloy design of NSSC EM-T were investigated in different temperature ranges. The studies and results are explained below.

4. Specimens and Test Methods

4.1 Specimens

Table 2 shows the chemical composition of the test materials. To clarify the effects of Mo, Cu, W and Nb on steel strength at room temperature and high temperature, their addition amounts to a low-C, low-N, 17–18Cr basic steel were changed. Specimen sheets were prepared by subjecting ingots of prescribed alloy compositions to solution treatment at 1 230°C for 2 h, hot rolling into sheets 4.5 mm in thickness, annealing at 1 050 to 1 100°C without soaking, cold rolling to a thickness of 2.0 mm and then annealing at 1 000 to 1 100°C so that the crystal grain size conformed to No. 6 defined in JIS G 0552.

4.2 Test methods

4.2.1 Tensile test at room temperature

The specimen sheets were cut into No. 13B test pieces under JIS Z 2201 so that the tensile force was applied in the rolling direction. The tensile test was conducted according to JIS Z 2241, the gauge length being set at 50 mm, the tensile force applied at a rate of 20 MPa/s up to the point of 0.2% proof stress and at 40 mm/min thereafter. Total elongation was determined by the butting method.

4.2.2 Tensile test at high temperature

The high temperature tensile test was conducted according to JIS G 0567. Flat test pieces 2.0 mm in thickness having a gauge length of 50 mm were heated for 15 min to the prescribed temperature, held there for 15 min for soaking and then subjected to the tensile test. The strain rate as defined between the gauge marks was controlled to 5×10^{-5}/s up to 0.2% proof stress, and thereafter, the crosshead speed was set at 3.0 mm/min.

4.2.3 Thermal fatigue test

The thermal fatigue test was conducted using two types of test pieces, round bars and pipes. The diameter of the round bar test pieces was 10 mm, and the distance between the gauge marks was 15 mm. The pipe test pieces were ERW pipes 38.1 mm in outer diameter and 2 mm in wall thickness, and the distance between the gauge marks was 15 mm. Note that, to prevent bulging during the test, the pipe test pieces were machined so that the wall thickness of the portion between the gauge marks was 1 mm. The round bar test pieces underwent the following heat cycles under a constraint ratio of 20%: heating to 1 000°C at a rate to 3°C/s, holding there for 2 min, cooling to 200°C at a rate to 3°C/s and then holding there for 30 s. Defining the stress at the time when a test piece is cooled to 200°C in the tenth cycle as the initial stress, the thermal fatigue life was judged to have expired when the stress decreased to 75% of the initial stress or less during a later cycle. The pipe test pieces were tested and evaluated under the same conditions as above except that the heating end temperature was set at 880 and 950°C for different test pieces.

Table 2 Chemical composition of test materials

(mass%)

C	Si	Mn	Cr	Nb	Mo	W	Cu	Ti	N
0.01	0.3	1.0	17–18	0.01–0.9	0.01–3.2	0.01–2.7	0.01–2.0	0.1	0.01

4.2.4 Oxidation test

Test pieces 2.0 mm in thickness, 25 mm in width and 35 mm in length were cut out, finished with emery paper to #600 in all the surfaces and then degreased with acetone. In the continuous oxidation test, the mass gain by oxidation of each test piece was measured after heating and holding at 950 or 1 000°C for 100 h in normal atmosphere in an electric furnace. In the cyclic oxidation test, the test pieces underwent heat cycles of heating to 950°C for 5 min and cooling for 5 min in normal atmosphere, and their mass gain was measured in every 500 cycles up to a maximum of 2 000 cycles.

5. Appropriate Addition Amounts of Alloy Elements

5.1 Effects of Nb, W and Mo on tensile strength at room temperature

Figure 3 shows the effects of the addition amounts of Nb, W and Mo on the 0.2% proof stress of 18Cr steel at room temperature. Strength increased with Nb addition by comparatively small amounts, and the strength virtually hit a peak with an Nb addition by approximately 0.7%. On the other hand, by increasing the addition of W or Mo, strength increased virtually monotonously, and no peak strength was detected even with the addition of either of them by 2.5% or more. The strength increase per 1% addition of Nb was 40 MPa, that of W 20 MPa and that of Mo 10 MPa, approximately; Nb and W proved to have greater strengthening effects.

5.2 Effect of Cu on 0.2% proof stress at 600 to 800°C

Precipitation hardening with Cu is applied for increasing steel strength in the medium temperature range of roughly 600 to 800°C.[2–4] **Figure 4** shows the effect of Cu content on the 0.2% proof stress of 17Cr-0.3Nb-0.15Ti steel at 600, 700 and 800°C.[3] At any temperature from 600 to 800°C, the proof stress tends to increase significantly when Cu addition exceeds 0.5%. It is clear from the above that, with Cu addition by 0.5% or more, the increase in 0.2% proof stress is 95 MPa per 1% addition of Cu at 600°C, 45 MPa at 700°C and 20 MPa at 800°C, approximately, which demonstrates the effectiveness of Cu for improving steel strength in the medium temperature range. It has been reported that in an environment where heating and cooling are repeated and strain is imposed like in that of exhaust manifolds, different from the condition of static aging, the particles of Cu precipitates do not grow by simple Ostwald growth but, rather, repeat fragmentation, solid solution and re-precipitation through interaction with dislocations, and by so doing, maintain their fine size.[2, 4] This seems to indicate that Cu can be effectively used for strengthening steel in the medium tempera-

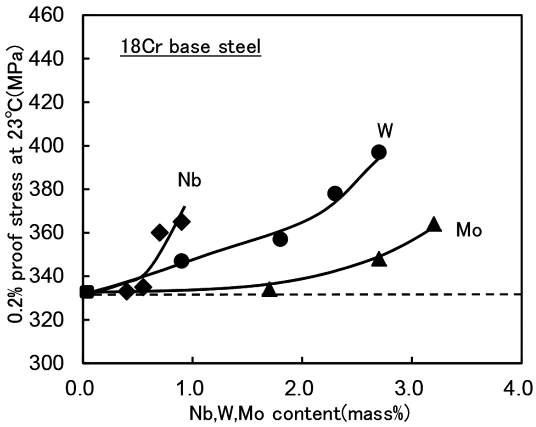

Fig. 3 Effect of Nb, W and Mo on 0.2% proof stress at room temperature

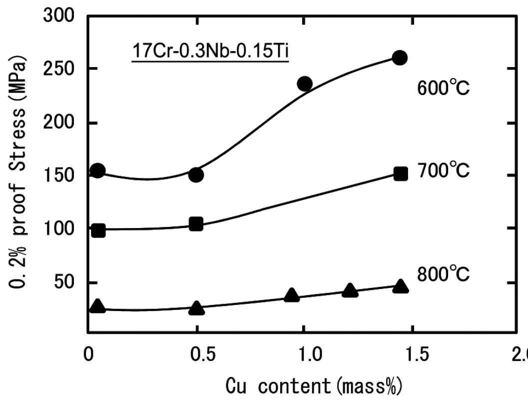

Fig. 4 Effect of Cu on 0.2% proof stress at 600, 700 and 800°C[3)]

ture range.

5.3 Effects of Nb, Mo and W on 0.2% proof stress at 950°C

Increasing the 0.2% proof stress in the tensile test at high temperature is effective at improving thermal fatigue properties, and there have been various studies on the effects of alloying elements on the proof stress at high temperature,[8)] but few of them deal with the effects in the temperature range of 950°C. **Figure 5** shows the effects of Nb, Mo and W on the 0.2% proof stress at 950°C. At this temperature, as long as the addition amount is roughly 1%, Nb, Mo and W exhibit steel strengthening effects in this descending order, and especially Nb improves high-temperature strength markedly with a relatively small addition amount. While Mo and Nb have been conventionally reported to contribute to the increase in high-temperature strength by solid solution hardening or precipitation hardening, W seems to exert the same strengthening effect also by the same mechanism.

5.4 Toughness at low temperature

As described earlier, the addition of Mo, Cu, W and Nb is effective at increasing steel strength at room temperature to high temperature, and it is suggested that the combined addition of two or more of them brings about greater effects. However, low-temperature toughness is adversely affected by high alloying, which may lead to problems in the commercial production of the steel. Studies have revealed that excessive addition of Mo deteriorates toughness,[9)] but there have been no such studies on W, and it was necessary to clarify the adequate amount of its addition. Thus, we investigated the adequate W addition amount that would not lead to problems in commercial production. **Figure 6** shows the effect of W on the Charpy impact value of hot rolled and annealed sheets. While the impact value decreases by increasing the W content, the target toughness value of 20 J/cm^2 or more can be achieved as long as the addition amount is 2.0% or less.

5.5 Thermal fatigue

Figure 7 shows the temperature-stress curves of the round bar specimens of the 18Cr-2Mo-1.5Cu-1.6W-0.5Nb steel and the type 444 at the tenth cycle of the thermal fatigue test at 200 to 1 000°C under a constraint ratio of 20%. Through comparison of the stress changes of the two steels, the stress of the former is higher than that of the latter on both the tensile side in the low to medium temperature range and the compressive side in the high temperature range. Whereas the value of $\Delta\varepsilon_p$ of the latter is 1.03, that of the former is 0.73 because of its higher strength at low to high temperature. It has thus been clarified that it is possible to markedly reduce $\Delta\varepsilon_p$ by increasing the steel strength in low to high temperature ranges. This

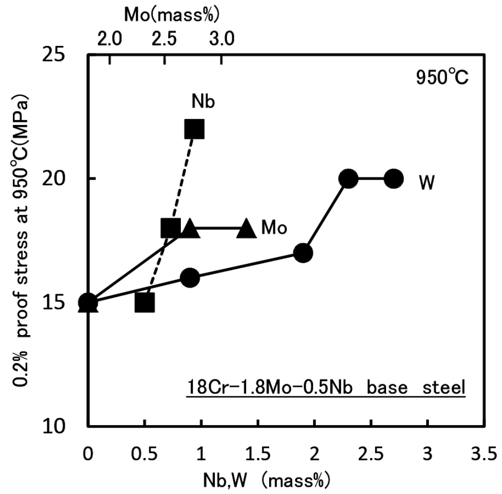

Fig. 5 Effects of Nb, Mo and W on 0.2% proof stress at 950°C

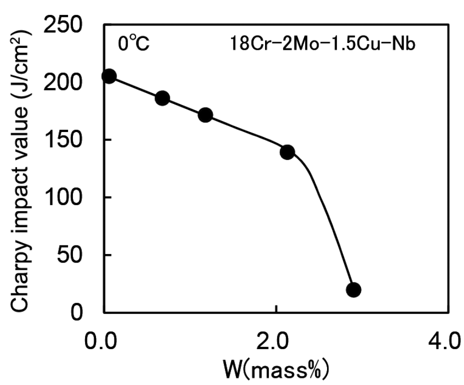

Fig. 6 Effect of W on Charpy impact value of 18Cr-2Mo-1.5Cu-Nb steel

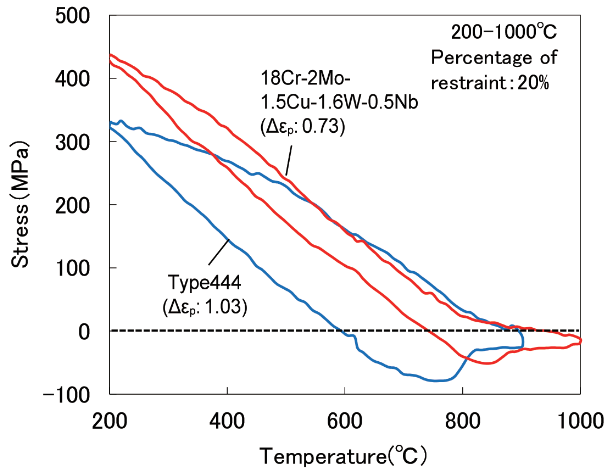

Fig. 7 Temperature-stress curves at tenth cycle of thermal fatigue test

presumably resulted from steel strengthening in the entire temperature range of use as a result of the following three: the solution strengthening with Nb and W in the low temperature range; the precipitation strengthening with Cu in the middle temperature range; and the solution strengthening with Nb, Mo and W in the high temperature range. **Figure 8** shows the thermal fatigue life of the two steels measured under the test condition. Whereas the thermal fatigue life of the conventional type 444 was 290 cycles, that of the developed steel was 670 cycles, more than twice in thermal fatigue properties.

Through the above studies, the adequate addition amounts of Mo, Cu, W and Nb to produce the desired thermal fatigue properties, the most important issue, without lowering productivity in commercial production have been defined. Based on these findings, the chemistry of NSSC EM-T has been determined as 17Cr-2Mo-1.5Cu-1.3W-0.5Nb to obtain high toughness at low temperature and excellent heat resistance. The characteristics of the developed steel are presented below.

6. Characteristics of Developed NSSC EM-T

6.1 Typical chemical composition and mechanical properties

Table 3 shows a typical chemical composition of NSSC EM-T; for comparison purposes, the same for type 444 is also shown. The mechanical properties and heat resistance performance of the two were compared using sheet specimens 2 mm in thickness manufactured through commercial facilities. **Table 4** shows the mechanical properties of the developed and comparative steels. NSSC EM-T has a 0.2% proof stress higher than that of the type 444 by roughly 100 MPa, and a tensile strength higher by roughly 50 MPa, both at room temperature. With respect to workability, the total elongation at the tensile test is 30% or more, and the average r-value is 1.0, not significantly lower than those of the type 444.

6.2 Mechanical properties of high-frequency ERW pipes

Table 5 shows the mechanical properties of high-frequency ERW pipes of NSSC EM-T after annealing, 38.1 mm in outer diameter and 2.0 mm in wall thickness. The 0.2% yield stress and tensile strength of the pipe specimens of NSSC EM-T are substantially the same as those of cold-rolled and annealed sheets of the same steel, and higher than those of the type 444. In addition, the total elongation (EL) of NSSC EM-T is 45%, which is not significantly lower than 48% of the type 444.

6.3 Tensile properties at high temperature

Figure 9 shows the high-temperature tensile properties of NSSC EM-T and the type 444 (the graph on the right-hand side is an enlargement of the high-temperature part of the graph on the left-hand side). The 0.2% proof stress of the former is higher than that of the latter at low to high temperature, which verifies the former's excellent high temperature strength. The main reason for the slightly higher strength of the former at 600°C is presumably the precipita-

Table 3 Typical chemical compositions of NSSC EM-T and Type444
(mass%)

Steel	C	Si	Mn	Cr	Nb	Mo	W	Cu	N
NSSC EM-T	0.01	0.3	0.8	17	0.5	2.0	1.3	1.5	0.01
Type444	0.01	0.2	1.0	18	0.6	2.0	–	0.1	0.01

Table 4 Mechanical properties of NSSC EM-T (specimen: JIS13B, RD)

Steel	0.2%PS (MPa)	TS (MPa)	EL (%)	r-value
NSSC EM-T	434	560	31	1.0
Type444	350	520	32	1.1

Table 5 Mechanical properties of ERW pipe (ϕ38.1 mm × 2 mmt)

Steel	0.2%PS (MPa)	TS (MPa)	EL (%)	Pipe expansion
NSSC EM-T	438	549	45	No cracks at 1.3D
Type444	376	519	48	No cracks at 1.3D

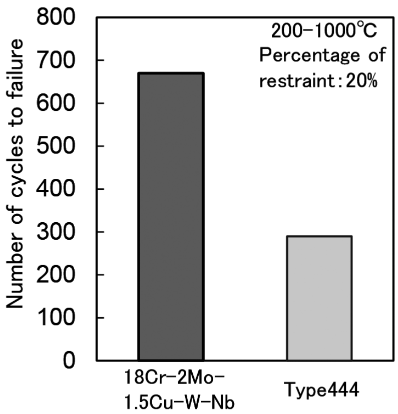

Fig. 8 Thermal fatigue life of round bar test pieces

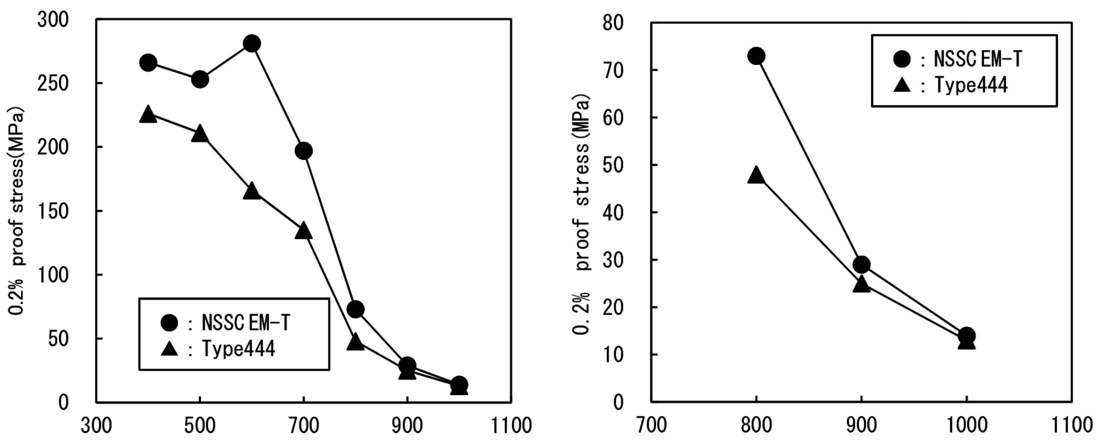

Fig. 9 Tensile properties at elevated temperatures of NSSC EM-T and Type 444

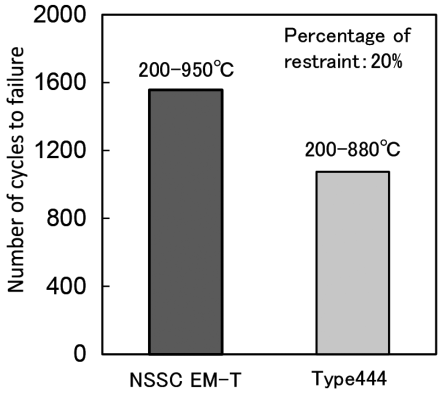

Fig. 10 Thermal fatigue life of ERW pipes of NSSC EM-T

tion hardening with Cu particles as stated earlier.

6.4 Thermal fatigue properties

Figure 10 shows the thermal fatigue test result of the ERW pipes of NSSC EM-T (200 to 950°C) and the type 444 (200 to 880°C) at a constraint ratio of 20%. NSSC EM-T proved to have a thermal fatigue life of 1557 cycles at 200 to 950°C, superior to that of the comparative type 444 of 1075 cycles at 200 to 880°C. The above results show that the target heat resistance temperature of 950°C, higher than that of the type 444 of 880°C, has been achieved by a margin of 70°C.

6.5 Oxidation at high temperature

Figure 11 shows the result of the continuous oxidation test of NSSC EM-T and the type 444 at 950 and 1000°C for 200 h. No breakaway oxidation or flaking of oxide scale was observed at either 950 or 1000°C. **Figure 12** shows the result of the cyclic oxidation test at 950°C. After 2000 cycles of heating at 950°C for 5 min and air cooling for 5 min, no abnormal oxidation or oxidation mass loss was found with NSSC EM-T, which proves its excellent resistance to high-temperature oxidation in an environment of repeated heating and cooling.

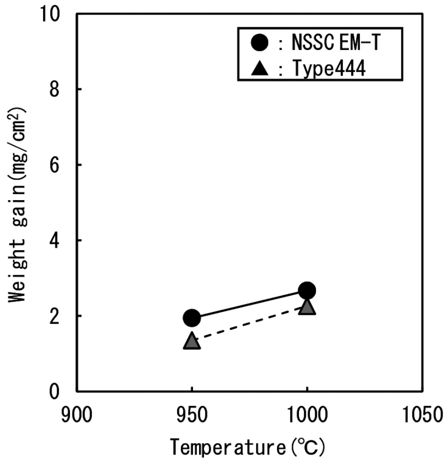

Fig. 11 Continuous oxidation test of NSSC EM-T

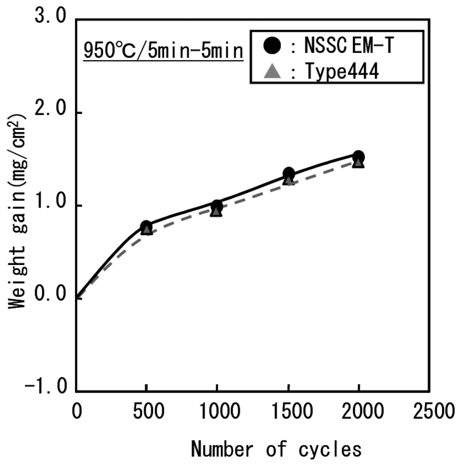

Fig. 12 Cyclic oxidation test of NSSC EM-T

7. Conclusion

The following findings were obtained through the studies for the present development.

(1) In terms of the increase in 0.2% proof stress per 1% addition of Nb, Mo, Cu and W as measured in the tensile test at room temperature, Nb and W proved to be more effective than the other two.

(2) To increase the 0.2% yield stress in the medium temperature range of 600 to 800°C, it is effective to add Cu by 1.0 to 1.5%. In the high temperature range of 950°C, in contrast, Nb and W proved to have higher strengthening effects.

(3) The effect of W on the low-temperature toughness of hot-rolled and annealed sheets of the developed 18Cr-2Mo-1.5Cu-Nb steel was examined, and the toughness was found to decrease significantly when the addition amount of W was more than 2.0%.

(4) The thermal fatigue life of NSSC EM-T pipes at 200 to 950°C under 20% constraint was markedly better than that of the comparative type 444 at 200 to 880°C, owing to smaller $\Delta\varepsilon_p$.

(5) The tensile properties of NSSC EM-T steel sheets and pipes at room temperature were better than those of the type 444, and the total elongation of the former was not significantly poorer.

(6) In either the continuous oxidation test at 950 and 1000°C or the cyclic oxidation test at 950°C, NSSC EM-T demonstrated no breakaway oxidation nor mass loss due to scale flaking, and excellent high-temperature oxidation characteristics were confirmed.

Based on the above study results, the optimum addition amounts of alloy elements were set at 2.0% Mo, 1.5% Cu, 1.3% W and 0.5% Nb, and the composition of the developed NSSC EM-T was defined as 17Cr-2Mo-1.5Cu-1.3W-0.5Nb. The developed steel maintains its excellent properties at 950°C, higher by 70°C than the heat resistance temperature of the type 444 series, 880°C.

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