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Development of Ferritic Stainless Steel YUS 450 with High Heat Resistance for Automotive Exhaust System Components

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Abstract:

To clean the automobiles' exhaust gases and improve fuel economy, measures have been implemented that raise exhaust-gas temperature and reduce body weight. Nippon Steel has developed a low-cost, high-heat resistant ferritic stainless steel, designated YUS 450 (14Cr-0.3Nb-0.1Ti-0.5Mo). According to the finding that adding niobium and titanium can simultaneously prolong thermal fatigue life, the most important property for exhaust manifold materials, and ensure stiffness during high-temperature service, despite thickness reduction, niobium and titanium are added in respective amounts of 0.3% and 0.1% to obtain high-temperature strength and prevent grain growth around 900°C. The chromium content is set at 14% to provide oxidation resistance at temperatures close to 900°C. According to another finding that corrosion thickness loss from hot salt damage can be reduced by a trace addition of 0.5% molybdenum. YUS 450 is superior to the conventional automotive exhaust system stainless steel SUS 430 J1L (YUS 180 with 19Cr-0.4Nb-0.4Cu) in high-temperature properties, such as thermal fatigue life and hot salt damage resistance, and can be produced at low cost by reducing the alloy content.

1. Introduction

In recent years, automobile manufacturers have been aggressively improving fuel economy and cleaning exhaust gases to protect the global environment[1]. Achieving higher gas mileage and cleaner exhaust gases requires lighter automobile weight and higher exhaust gas temperature. For this reason, higher heat resistance is required of exhaust system materials. For the exhaust manifold located below the engine, conventional cast iron is being replaced by a thinner stainless steel sheet or cast structure to increase heat resistance[2]. A sheet structure is more advantageous than a cast structure in terms of thickness reduction. Thermal fatigue strength is most important to the life of the exhaust manifold. When the exhaust manifold is reduced further in section thickness, it requires higher stiffness and corrosion resistance during high-temperature service. High-temperature strength and hot salt damage resistance are important for ensuring desired stiffness

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and perforation resistance, respectively. Stainless steel exhaust manifolds perform better than cast iron manifolds, but are more costly. This cost must be reduced for commercial application.

The authors have studied the roles of alloying elements and developed a 14% chromium ferritic stainless steel, designated YUS 450, with high-temperature properties superior to those of the conventional automobile exhaust system stainless steel SUS 430 J1L (YUS 180 with the 19Cr-0.4Nb-0.4Cu composition), by adding niobium, titanium, and molybdenum while limiting the total alloy content.

2. Experimental Methods

The chemical composition ranges of steel samples are listed in **Table 1**. Eight kilograms of each sample was melted in a high-frequency vacuum furnace, cast into a slab, heated to 1,250°C, hot rolled, cold rolled, and annealed at 800°C to 950°C into a 2-mm thick sheet. To evaluate changes in properties when actually used in cars, the samples were heated (aged) at 900°C for a long time. The annealed samples and the aged samples were hot-tension tested and microstructurally analyzed to determine high-temperature strength and microstructural stability during high-temperature service. The hot-tension test was conducted at 900°C with collared sheet specimens as described in Japanese Industrial Standards (JIS) G 0567. The effect of molybdenum was investigated by using titanium-molybdenum and niobium-molybdenum steels in which carbon and nitrogen were tied up to prevent them from hardening with martensite formation.

For precipitates, the extraction residue produced by the potentiostatic electrolysis method was identified and determined by chemical analysis and X-ray diffraction. For microstructures, extraction replicas were observed mainly by transmission electron microscopy and analyzed for precipitates by energy-dispersive X-ray spectroscopy (EDS) and electron diffraction. The annealed samples to be formed into exhaust system components were tested for hot salt damage and thermal fatigue properties. One cycle of the hot salt damage test comprised holding the samples at 600°C to 750°C for two hours, cooling in air, and immersing in a saturated sodium chloride (NaCl) solution for five minutes. The specimens were tested for a maximum of 40 cycles, and their weights before and after the test were measured.

The optimum chemical composition was determined from the above-mentioned test results. Cold-rolled and annealed 2-mm thick specimens were produced at the mill and compared with the conventional SUS 430 J1L in terms of thermal fatigue strength, loss of high-temperature strength as a result of aging, hot slat damage resistance, oxidation resistance, and formability. In the thermal fatigue test, 2-mm thick sheet specimens were restrained by 100%, cyclically heated at 900°C and cooled to 200°C, and judged to have failed when their load dropped to 10% of the maximum load. Oxidation resistance was evaluated by continuous heating and intermittent heating. In the continuous heating test, the specimens were continuously heated for 200 hours in an atmosphere of wet air with a dew point of about 30°C, and their weights before and after the test were measured. In the intermittent heating test, the specimens were furnace heated for 30 minutes and air cooled for 15 minutes. Their weights were measured every 30 cycles, and the test was run to 300 cycles.

Table 1 Chemical composition ranges of steel samples (mass%)

C	N	Cr	Ti	Nb	Mo
0.01	0.01	11-15	tr.-0.5	tr.-0.6	tr.-2

Si:0.4-1.0, Mn:0.2-1.0, P:0.01-0.03, S<0.006

3. Experimental Results and Discussion

3.1 Effects of alloying elements niobium and molybdenum on high-temperature strength

Fig. 1 shows the effects of niobium and molybdenum on the 0.2% offset yield strength at 900°C of 13% chromium steel. Niobium does not change the 0.2% offset yield strength at 900°C when its content is up to 0.2%. Niobium does increase the 0.2% offset yield strength at 900°C as its content increases above 0.2%. Molybdenum increases the 0.2% offset yield strength at 900°C with increasing content, but its strengthening capability per unit addition is about one-fifth that of niobium.

Fig. 2 shows the relationship between the niobium and molybdenum additions and the solute niobium and molybdenum contents determined from electrolytic extraction residue. Niobium is slightly dissolved when added in an amount up to 0.2% and

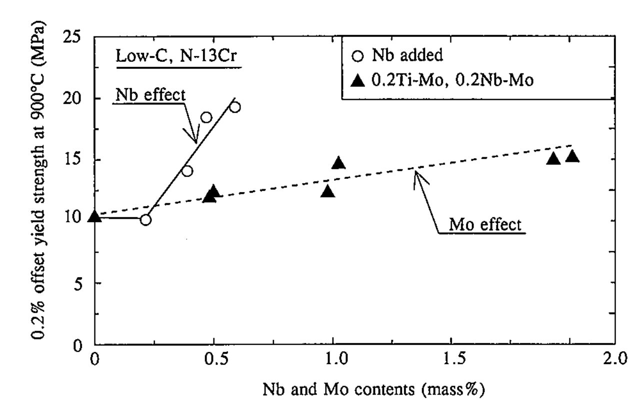


Fig. 1 Effects of niobium and molybdenum on 0.2% offset yield strength of 13Cr steel at 900°C

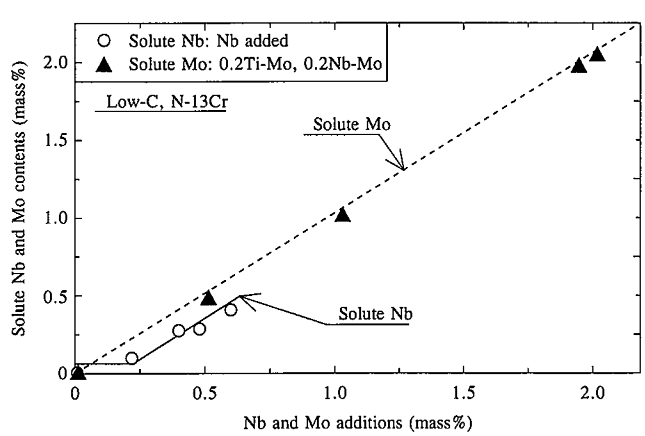


Fig. 2 Relationship between total amounts of niobium or molybdenum and contents of those elements in solution

starts to go into solution when its addition exceeds 0.2%. This may be explained by the formation of niobium carbonitrides, Nb(C,N), to niobium additions up to 0.2%. This relationship between the solute niobium content and the niobium addition agrees well with that between the 0.2% offset yield strength at 900°C and the niobium addition. The effect of niobium on the 0.2% offset yield strength at 900°C depends on solute niobium[3,4].

Molybdenum precipitates were not observed in the electrolytic extraction residue, and almost all of the molybdenum added was found to be in solution. This result suggests that the strength increase brought about by the addition of molybdenum derives from solute molybdenum[4,5].

3.2 Strength decrease and microstructural stability during high-temperature service

As discussed above, the contributors to strengthening at elevated temperatures are solute niobium and solute molybdenum; solute niobium is especially effective. However, niobium is so reactive that it forms precipitates during high-temperature service, probably reducing the amount of solute niobium available as a strengthener. As a result, there is concern the steel may lose strength and stiffness. The 0.2% offset yield strength and the solute niobium content after aging at elevated temperatures were investigated by simulating an actual service environment. **Fig. 3** superimposes the 0.2% offset yield strength at 900°C of steel aged at 900°C for 500 hours on the relationship between the 0.2% offset yield strength at 900°C and the niobium addition (see **Fig. 1**). Aging lowers the 0.2% offset yield strength at 900°C of 0.5% Nb steel to that of niobium-free steel. **Fig. 4** shows the relationship between the niobium addition and the solute niobium content of two annealed steels and one aged steel. Aging reduces the solute niobium content of each steel. This result also implies that the decrease in the solute niobium content is responsible for the loss of the 0.2% offset yield strength at 900°C after aging.

The precipitates observed by transmission electron microscopy in 0.5% Nb steel annealed and 0.5% Nb steel aged at 900°C for 500 hours are shown in **Photo 1**(a) and (b), respectively. The solute niobium content of each steel is included. Carbide of the M_6C type (Fe_3Nb_3C), measuring 1 μm or less in particle size, and Laves phase of the Fe_2Nb type are recognized in the annealed 0.5Nb steel. Markedly coarsened M_6C carbide particles are recognized in the aged 0.5% Nb steel. From these observations, it is inferred that aging precipitated and coarsened the M_6C carbide, which in turn consumed the solute niobium and lowered the 0.2% offset yield strength at 900°C. The loss of strength owing to aging is thus considered preventable by suppressing the precipitation of coarse M_6C.

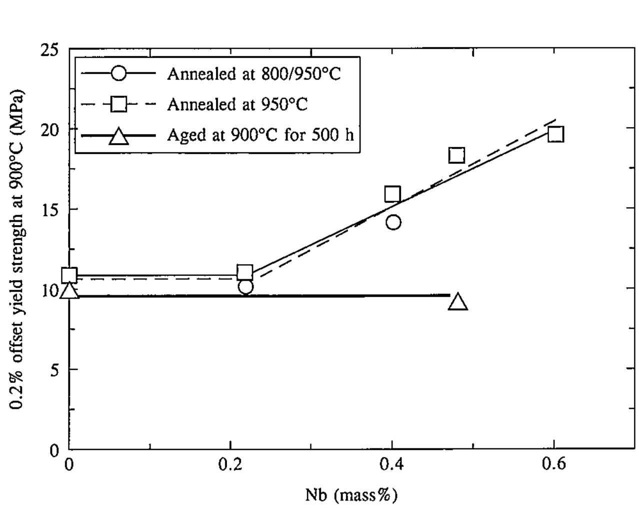


Fig. 3 Effect of niobium on 0.2% offset yield strength at 900°C of annealed and aged 13Cr steel

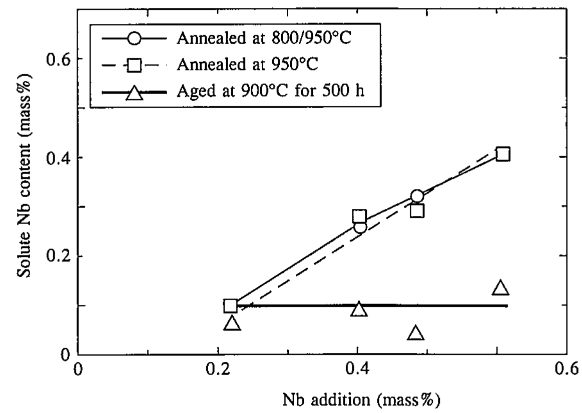


Fig. 4 Relationship between solute niobium content and niobium addition of annealed and aged 13% Cr steel

The precipitation of M_6C can be retarded by adding carbon in the smallest possible amount or tying up carbon with an element other than niobium. The former method increases the steelmaking cost, however. For this reason, the latter method was employed. Carbides of niobium are higher in free energy of formation than those of zirconium, tantalum, and titanium, among other elements[6]. In other words, when niobium coexists with these elements, it is presumed that carbon preferentially combines with the elements to retard the precipitation of niobium carbides. For this reason, titanium was selected as a cost-effective element to be added with niobium. Niobium-titanium-microalloyed steel (0.3Nb-0.1Ti-0.5Mo) was examined for precipitates in the annealed and aged conditions. The results are shown in **Photo 1**(c) and (d). Titanium and niobium carbonitrides (Ti,Nb)(C,N) are observed in the annealed Nb-Ti steel as shown in **Photo 1**(c). Titanium and niobium carbonitrides (Ti,Nb)(C,N) and Laves phase are observed in the aged Nb-Ti steel as shown in **Photo 1**(d). In this way, the addition of titanium with niobium was found to restrict the precipitation of coarse M_6C. The content of solute niobium as a strengthener is higher in the Nb-Ti steel than in the Nb steel after aging. The Nb-Ti steel is thus thought to be superior in stiffness during high-temperature service.

Because titanium is added to tie up carbon in advance of niobium as noted above, titanium must be added in an amount about four times as large as carbon and nitrogen in the steel of interest. Generally, ferritic stainless steels microalloyed with niobium or titanium have the combined carbon and nitrogen content lowered to about 0.02%, so that a titanium addition of about 0.1% is required. Niobium had to be added to niobium-microalloyed steel in amounts of 0.4% to 0.5% to maintain high-temperature strength. Because titanium ties up carbon and nitrogen in niobium-titanium-microalloyed steels, about 0.2% of niobium that precipitates as carbonitride and does not go into solution becomes

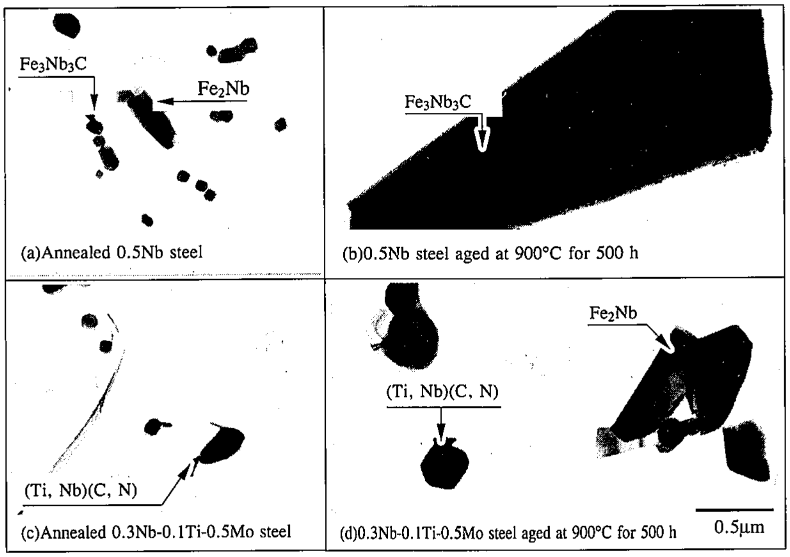


Photo 1 Precipitates observed by transmission electron microscopy and solute niobium content in annealed and aged 0.5Nb steel and 0.3Nb-0.1Ti-0.5Mo steel

unnecessary (see **Fig. 2**) and an addition of about 0.3% of niobium is sufficient.

3.3 Effects of alloying elements on hot salt damage

Because hot salt damage is almost uniform general corrosion, the average corrosion thickness loss was taken as an index of hot salt damage resistance. **Fig. 5** shows the effect of the chromium content on the corrosion thickness loss at 700°C. Chromium has no great influence on the thickness loss as its content increases. This means that chromium only slightly improves the hot salt damage resistance. The chromium content should be as low as possible in terms of formability and cost, but should be at least 14% to maintain oxidation resistance near 900°C[7]. Niobium and titanium affect the corrosion weight loss to a small degree. The effect of molybdenum on the corrosion weight loss is shown in **Fig. 6**. Molybdenum is particularly effective at the high end of the service temperature range where corrosion is severe. Molybdenum also contributes to an improvement in hot salt damage resistance when its addition is about 0.5%.

Based on the above results, 14Cr-0.3Nb-0.1Ti-0.5Mo was selected as the optimum chemical composition of the new ferritic stainless steel YUS 450.

3.4 Properties of YUS 450

The properties of the conventional steel SUS 430 J1L (YUS 180 with 19Cr-0.4Nb-0.4Cu) and the new steel YUS 450 (14Cr-0.3Nb-0.1Ti-0.5Mo), both produced at the mill, are compared.

Fig. 7 compares the change in the high-temperature strength of the steels when aged at 900°C. High-temperature strength before aging is the same for the two steels, but high-temperature strength after aging is higher for YUS 450 than for SUS 430 J1L. This means that YUS 450 is stiffer than SUS 430 J1L during high-temperature service. **Fig. 8** shows the thermal fatigue life of the two steels. YUS 450 lasts about 1.3 times longer than SUS 430 J1L. **Fig. 9** shows the hot salt damage resistance of the steels. The addition of molybdenum makes the corrosion thickness loss of YUS 450 smaller than that of SUS 430 J1L.

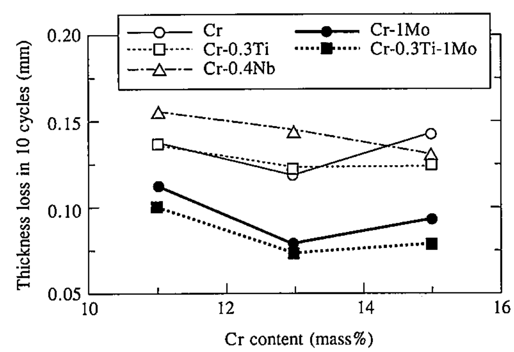


Fig. 5 Effect of chromium on corrosion thickness loss at 700°C

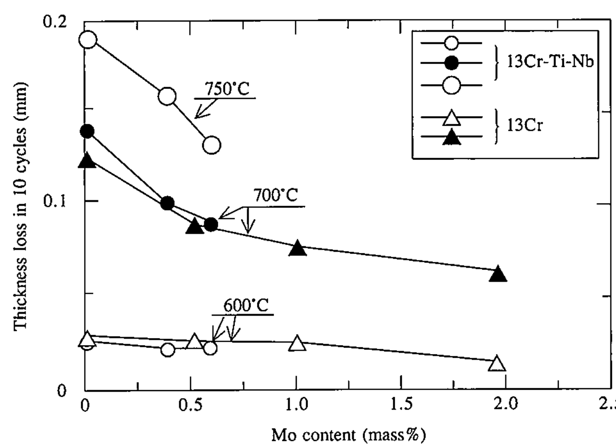


Fig. 6 Effect of molybdenum on corrosion thickness loss at 600°C to 750°C

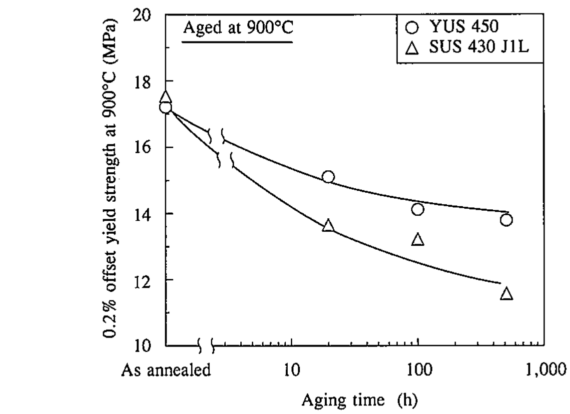


Fig. 7 Change in high-temperature strength of YUS 450 with aging at 900°C

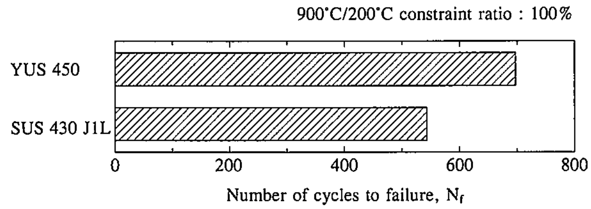


Fig. 8 Thermal fatigue life of YUS 450

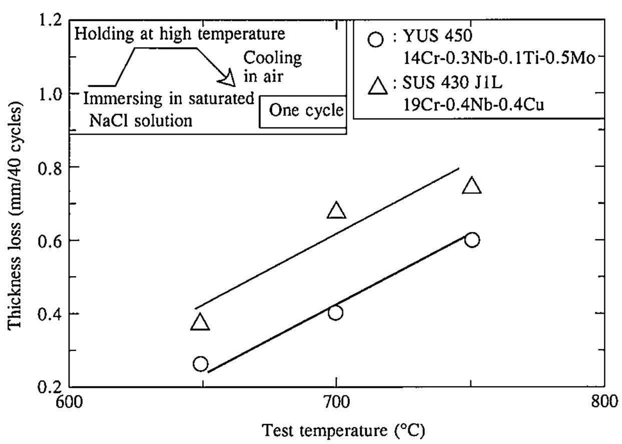
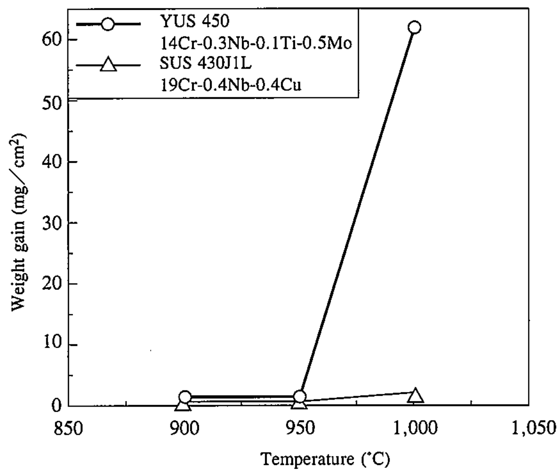
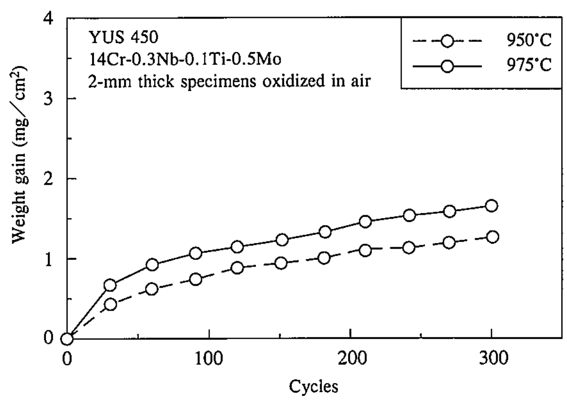


Fig. 9 Hot salt damage resistance of YUS 450



(a)Results of 200-h continuous oxidation test in atmosphere with dew point of 30°C



(b)Results of intermittent oxidation test in air

Fig. 10 Oxidation resistance of YUS 450

Table 2 Chemical composition and room-temperature mechanical properties of YUS 450

Steel	Cr	Nb	Ti	Mo	Cu	0.2% offset yield strength	El.	r value
YUS 450	14	0.3	0.1	0.5	-	320MPa	34%	1.2
SUS 430 J1L	19	0.4	-	-	0.4	340MPa	32%	0.9

Thickness: 2 mm

Fig. 10 shows the oxidation resistance of YUS 450 compared with SUS 430 J1L. When continuously annealed for 200 hours in an atmosphere with a dew point of 30°C as shown in **Fig. 10**(a), YUS 450 has maximum oxidation weight gain of about 2 mg/cm² at 950°C or less and suffers no nodule oxidation. When YUS 450 is intermittently oxidized in air to 300 cycles as shown in **Fig. 10**(b), its oxidation weight gain-time relationship at 975°C follows the parabolic law, suggesting no removal of the oxide film. YUS 450 does not suffer from nodule oxidation either.

Table 2 lists the chemical composition and room-temperature mechanical properties of YUS 450 and SUS 430 J1L. YUS 450 has small additions of titanium and molybdenum, contains copper, chromium, and niobium in smaller amounts than SUS 430 J1L, and thus has lower in steelmaking cost. YUS 450 is also reduced in yield strength, improved in ductility, and increased in the r value, which is an index of formability. The cost of fabricating parts from YUS 450 is expected to be lower than for SUS 430 J1L.

YUS 450 has carbon tied up by a small addition of titanium as discussed above, so that it can obtain a sufficient amount of solute niobium contributing to strengthening during high-temperature service for a long period of time. It thus excels in thermal fatigue properties and has a smaller loss of stiffness. The addition of molybdenum offers resistance to perforation by hot slat damage. YUS 450's chromium, copper, and niobium contents are lower than those of SUS 430 J1L, and its alloy cost is low as well. Thanks to these excellent properties, YUS 450 is being used in automobile exhaust system components.

4. Conclusions

1)To improve high-temperature yield strength, it is important to obtain desired amounts of solute niobium and molybdenum.

2)The combined addition of niobium and titanium inhibits the precipitation of coarse M_6C during aging at 900°C and ensures high-temperature strength during high-temperature service. The combination also prolongs thermal fatigue life.

3)The addition of molybdenum improves hot salt damage resistance. When added in as small an amount as 0.5%, molybdenum shows its effectiveness at the high end of the service temperature range.

4)YUS 450 with the optimum composition 14Cr-0.1Ti-0.3Nb-0.5Mo has been developed as a new ferritic stainless steel with thermal fatigue life, hot salt damage resistance, and microstructural stability during high-temperature service superior to those of conventional SUS 430 J1L.

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