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Heat-Resistant Austenitic Stainless Steel

Shinya YAMAMOTO* Yoshitaka NISHIYAMA
Yuichi FUKUMURA

Abstract

A newly heat-resistant austenite stainless steel "AH" series has been developed for high temperature up to 1,000˚C. It is introduced a characteristic and an application example about AH-4 which is especially high flexibility in this series.

1. Introduction

With growing concern about global warming and other environmental problems over the last few years, minimizing CO_2 emissions has become an important challenge calling for technical developments. At power plants burning fossil fuels, for instance, a higher boiler temperature is envisaged to raise efficiency, and as a consequence, materials constituting power plant equipment must be able to effectively withstand increasingly severe conditions.

Heat-resistant austenitic stainless steels excelling in oxidation resistance have been widely used for such high-temperature applications, typically as high-Cr, high-Ni steels including JIS SUS310S (25%Cr-20%Ni) and Alloy 800H (21%Cr-32%Ni), and as high-Si steels including JIS SUSXM15J1 (18%Cr-13%Ni-4%Si) series steels. These materials, however, are not totally satisfactory in terms of surface oxidation film adhesion, high-temperature strength or weldability, leading to a search for steels offering better high-temperature properties. In addition, since the steels mentioned above contain Ni and other rare metal elements they are expensive, so decreasing the need for such alloy elements is required for economic reasons.

In response, Nippon Steel & Sumitomo Metal Corporation has developed a new series of heat-resistant austenitic stainless steels (the "AH series") usable at temperatures exceeding 1,000˚C (see **Fig. 1**).

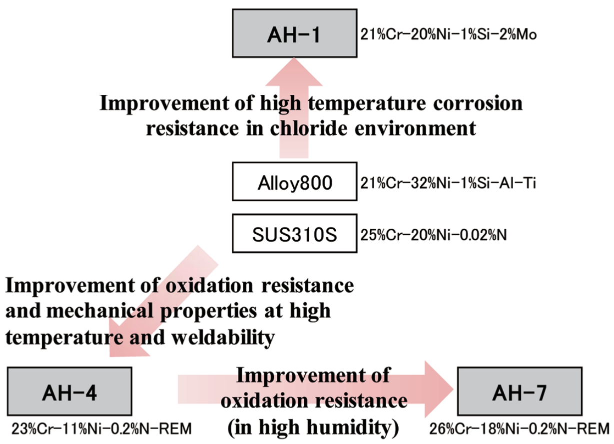

Fig. 1 Heat-resistant austenite stainless steel "AH" series

2. Basic Information on AH Series Steels

2.1 NSSMC-NAR-AH-1 ("AH-1" for short)

Alloy 800 having a high content of Ni has been used in high-temperature environments containing chlorides. To find a replacement, and working with then-Matsushita Electric Co. Ltd. (now Panasonic Corporation), Nippon Steel & Sumitomo Metal co-developed AH-1 (21%Cr-20%Ni-1%Si-2%Mo). To reduce cost, its Ni content is roughly 12% lower than that of Alloy 800, , and Mo is added to improve corrosion resistance. It is superior to Alloy 800 in terms of oxidation resistance, and corrosion resistance in high-temperature environments containing chloride, and also in terms of formability, weldability, and structural consistency after protracted heating. It is used mainly for sheathed heaters.

2.2 NSSMC-NAR-AH-4 ("AH-4" for short)

This steel was developed jointly with IHI Corporation,[1)] and is the most versatile of the AH series steels. While its Ni content is approximately 10% lower than that of JIS SUS310S, an austenitic stainless steel, it demonstrates superior high-temperature strength and oxidation resistance. It is used as a substitute for SUS310S for high-temperature applications at various power plant facilities and industrial furnaces. It is used also for automotive exhaust systems. More details on AH-4 are given in Section 3 hereof.

2.3 NSSMC-NAR-AH-7 ("AH-7" for short)

Exhaust gas recovery is an effective way to save energy. It is commonly practiced by heating fuel gas and combustion air through heat exchangers, using the heat of exhaust gas. However, the exhaust gases of some fuels contain water vapor in high concentra-

* Seninor Manager, Specialty Stainless Steel Technical Service & Solution Dept., Titanium & Specialty Stainless Steel Unit
2-6-1 Marunouchi, Chiyoda-ku, Tokyo 100-8071

tions, and cases have been seen where materials such as SUS 310S and AH-4 are quickly corroded. AH-7 (26%Cr-18%Ni-0.2%N-REM) is characterized by excellent oxidation resistance in hot and humid environments up to 1,000˚C.[2)] As evidence, **Photo 1** shows oxidation films that formed on the surfaces of AH-7 and SUS 310S during use in a combustion gas environment at 900˚C which contained 16% H_2O. The oxidation film of AH-7 is thinner than that of SUS 310S, but nonetheless, it is effective at suppressing local advances of corrosion. In addition, AH-7 is as effective as AH-4 in terms of tensile and creep rupture strengths at high temperatures.

Due to these excellent properties, AH-7 began to be used for fuel reformers for fuel cells, heat exchangers (regenerators) for new-generation gas turbines, inner linings for annealing furnaces, and other uses in steelmaking facilities.

3. Austenitic Stainless Steel NSSMC-NAR-AH-4 for Heat-resistant Uses

The characteristics, properties and applications of the AH steel series are presented below.

3.1 Alloy design philosophy

AH-4 was developed for applications for structural members used in high-temperature environments, and for these reasons, the design pursued excellent resistance to oxidation at high temperatures, erosion resistance, creep rupture strength, microstructural stability, cost efficiency, and weldability. **Figure 2** summarizes the alloy design philosophy at the development stage.

Oxidation resistance at high temperatures: Oxidation resistance depends on the formation of oxide films on the steel surface. It is widely known that the addition of Cr, Si and Al is effective in the formation of protective oxidation films at high temperatures. However, Si makes steel more sensitive to weld cracks, and Al is detrimental to creep properties when N coexists. To compensate, rare-earth metals, La and Ce, were added to suppress the growth and flaking off of oxide films, to provide better oxidation resistance at high temperatures.

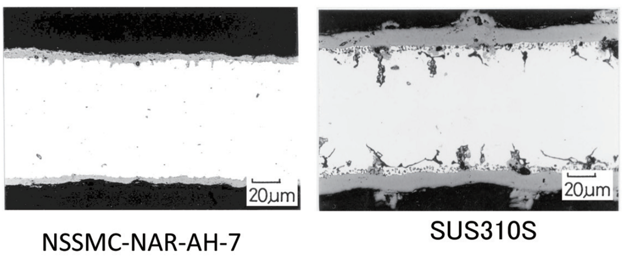

Photo 1 Cross sections of heat exchanger tubes after oxidation test ($3\%O_2$-$9\%CO_2$-$16\%H_2O$-bal.N_2, 900˚C × 500 h)

Creep rupture strength: Solid solution hardening, precipitation hardening, and crystal grain coarsening are widely known to be effective at improving creep rupture strength. The developed steel is solid solution hardened through the addition of N. Additionally, grain boundaries are strengthened by the addition of a small amount of B, and Al is added by a prescribed small amount to coarsen crystal grains.

Microstructural stability and weldability: To prevent the deposition of brittle structure (such as the σ phase), it is necessary to stabilize the austenitic structure. Although Ni is effective at stabilizing the austenitic phase, it is expensive, and deteriorates weld crack sensitivity. On the other hand, N, which is added for solid solution hardening purposes as mentioned earlier, is effective also in stabilizing the austenitic structure. Structural stability and good weldability have been obtained by adequately controlling the amount of N, by decreasing the amount of Si (which deteriorates weld crack sensitivity), and by controlling the amount of Ni added at the same time so that the relationship between the Cr equivalent and the Ni equivalent falls within an optimum range.

3.2 Properties of AH-4

Table 1 compares a typical chemical composition of AH-4 with that of SUS 310S.

The Ni content of AH-4 is roughly 10% less than that of SUS 310S, making AH-4 more economical. It contains N at roughly 0.2% for solid solution hardening, La and Ce (rare-earth metals) at roughly 0.03% in total to improve resistance to oxidation at high temperatures, and B at roughly 30 ppm to strengthen grain boundaries in order to raise creep rupture strength.

3.2.1 Oxidation resistance at high temperatures, and erosion resistance

The results of isothermal oxidation tests at 900 and 1,000˚C for 200 hours for AH-4 and SUS 310S are given in **Fig. 3**. The ordinate represents the total mass gain of the specimens, including the oxide film which flaked off during the test; the figure corresponds to the mass of oxygen in the oxide films. The oxide films of AH-4 are sta-

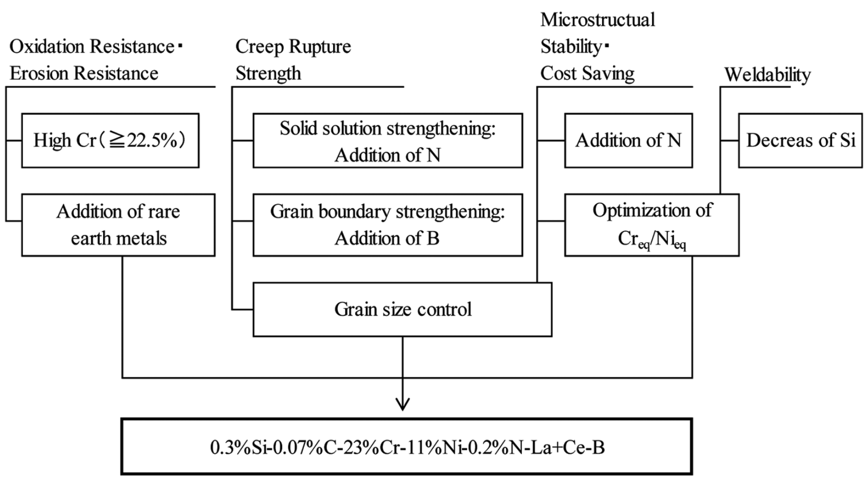

Fig. 2 Alloy design of developed austenitic stainless steel, NSSMC-NAR-AH-4

ble and adhesive in either of the temperature ranges, and its mass gain is less than half that of SUS310S, which demonstrates the excellent oxidation resistance of AH-4 at high temperatures.

Figure 4 shows the results of erosion tests on the two steels at 900˚C. As also demonstrated in the high-temperature oxidation tests, AH-4 was found to be superior to SUS310S in terms of maximum thickness loss, thanks to stable and adhesive protective oxide films, and thus its weight loss is roughly one-third that of SUS310S.

3.2.2 High-temperature strength and creep rupture strength

The results of tensile tests on the two steels at 800 to 1,000˚C are given in **Fig. 5**. AH-4 is superior to SUS310S in terms of both 0.2% yield strength and tensile strength. The results of creep rupture tests at 900 and 1,000˚C are shown in **Fig.6**. The creep rupture strength of AH-4 is approximately twice that of SUS310S as a result of solid solution hardening by nitrogen addition, grain size control, and grain boundary strengthening by boron addition.

Table 1 Chemical compositions of specimens (mass%)

Alloys	C	Si	Mn	P	S	Cr	Ni	La+Ce	B
NSSMC-NAR-AH-4	0.07	0.31	0.48	0.021	0.001	23.11	10.95	0.03	0.003
SUS310S	0.05	0.58	1.21	0.023	0.001	24.63	20.25	–	–

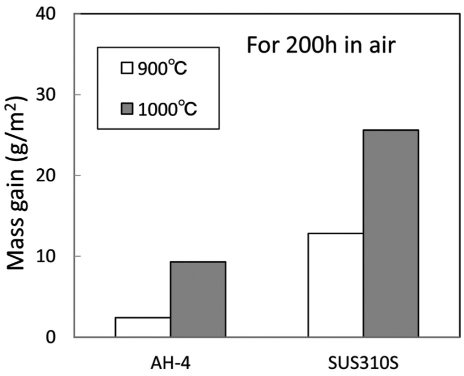

Fig. 3 Isothermal oxidation test result (200 h)

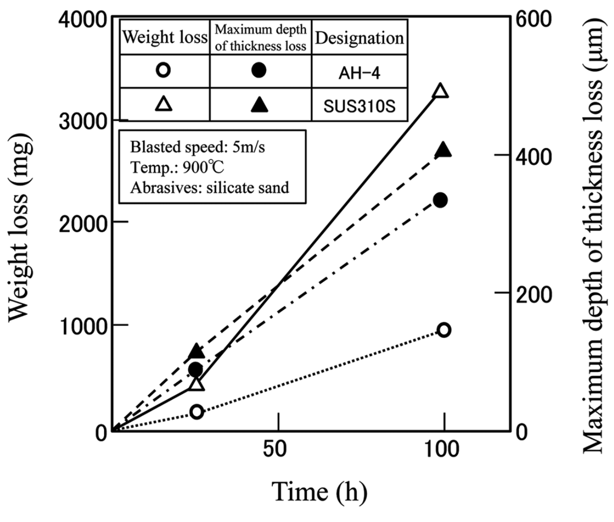

Fig. 4 Erosion test result (900˚C)

3.2.3 Microstructural stability

Figure 7 shows Charpy impact test results of the steels after aging for 3,000 h at 700 to 900˚C, the temperature range where the σ phase precipitates most easily. Whereas the σ phase precipitated in SUS310S at 800 and 900˚C, causing its impact value to fall, the impact value of AH-4 remained high.

3.2.4 Weldability

With respect to weld crack sensitivity at high temperatures, **Fig.**

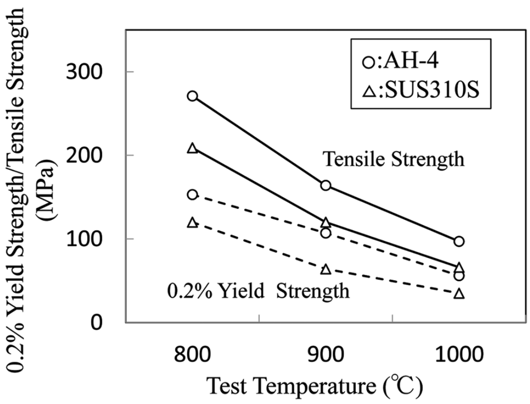

Fig. 5 Tensile properties at high temperature

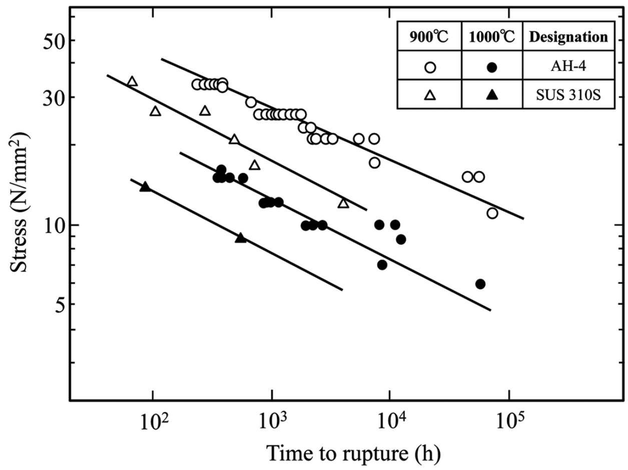

Fig. 6 Creep rupture properties

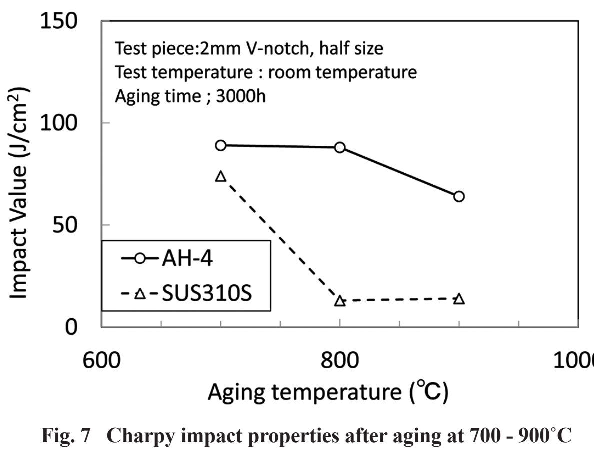

Fig. 7 Charpy impact properties after aging at 700 - 900˚C

8 shows the results of Longitudinal Varestraint tests on the two steels. Cracking occurred in SUS310S, but it occurred only a little in AH-4, thanks to the reduced content of Si and Ni.

3.3 Applications

As shown in Sub-section 3.2 above, AH-4 is superior to SUS310S in terms of high-temperature strength, creep rupture strength, structural stability, and weldability. These excellent properties of AH-4 are very effective especially in applications for structures requiring deformation resistance at high temperatures. Thanks also to its high cost efficiency due to its low Ni content, AH-4 has been used for various structures requiring high-temperature use.

Table 2 shows an assessment of AH-4 applications in different environments. In either oxidizing or reducing atmospheres, AH-4 deformation and thickness loss are less than those of SUS310S, and therefore AH-4 deformation and thickness loss deformation are less than in SUS310S, and therefore its service life is generally longer. At 1,000°C and above, however, its superiority in deformation resistance becomes less significant, its service life becomes substantially the same depending on other environmental conditions, and its cost efficiency remains as the only outstanding advantage. On the other hand, in carbon-containing atmospheres, depending on the gas chemistry the service life of AH-4 may be shorter than that of SUS310S. This is presumably because of the low Ni content and consequent poorer resistance to carburization. As stated above, when examining the applicability of AH-4 it is important to examine usage conditions beforehand.

Typical applications of AH-4 are presented below.

3.3.1 Burners and industrial furnaces

(1) Burners

At Wakayama and Kashima Works of Nippon Steel & Sumitomo Metal, drying/heating burners for torpedo ladle cars are inserted inside the vessel, so they must be resistant to oxidation and creeping, and also excellent in strength at high temperatures. SUS310S was once used for the burners, but they began to exhibit deformation and thickness loss after about two years of use and had to be replaced with new ones within three to five years. **Photo 2** shows a burner made of AH-4 after two years of use. The AH-4 burner seems to have suffered little thickness loss from corrosion caused by high-temperature oxidation, and demonstrates little deformation.

(2) Industrial furnaces

Muffle furnaces are used when it is necessary to control the furnace atmosphere during heat treatment or baking. AH-4 is being used in trials for the muffles proper and other components of some furnaces; **Photo 3** shows a muffle tube made of AH-4. Thanks to its excellent high-temperature properties, AH-4 muffle service life is longer than that of SUS310S muffles because of less deformation and thickness loss.

3.3.2 Power plants, etc.

(1) PFBC boilers and coal-fired power plants

AH-4 was developed jointly with IHI as mentioned earlier; the initially envisaged application was for pressurized fluidized-bed combustion (PFBC) boilers. Coal ash as hot as 800 to 900°C is fluidized in the ducts and cyclones of this type of boiler, and their material is required to be highly resistant to oxidation and erosion in that temperature range. Upon development, AH-4 was used for the boiler components, and proved superior to SUS310S and high-silicon stainless steel. In view of the excellent high-temperature properties thus demonstrated, AH-4 was then used for such applications as

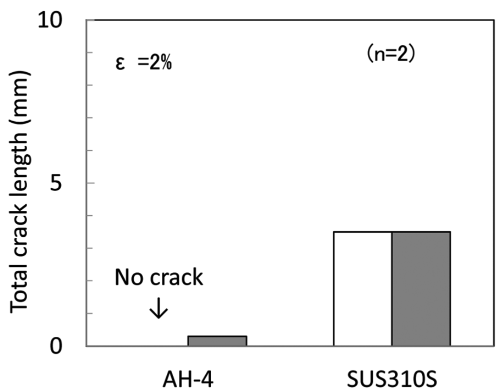

Fig. 8 Longitudinal-Varestraint test for hot crack susceptibility

Photo 2 Burner for torpedo car used for 2 years

Table 2 Lifetime assessment of NSSMC-NAR-AH-4 for various environment

Environment	Burner, industrial furnace	Remarks
Oxidizing atmosphere	◎ Burner for torpedo car ◎ Smelting container	Good resistance of oxidation and mechanical properties at high temp.
Reducing atmosphere	◎ Anchor of refractory △ ~ ◎ Muffle furnace ◎ Parts in the furnace	Good mechanical properties at high temp. Predominancy reduced above 1,000°C
Carbon content atmosphere	× Muffle furnace △ Parts in the furnace	Depending on temp. and gas composition, resistance of carburization is inferior for low nickel. → Prior test is required.

As compared with current material lifetime ◎ : Longer, △ : Same, × : Shorter

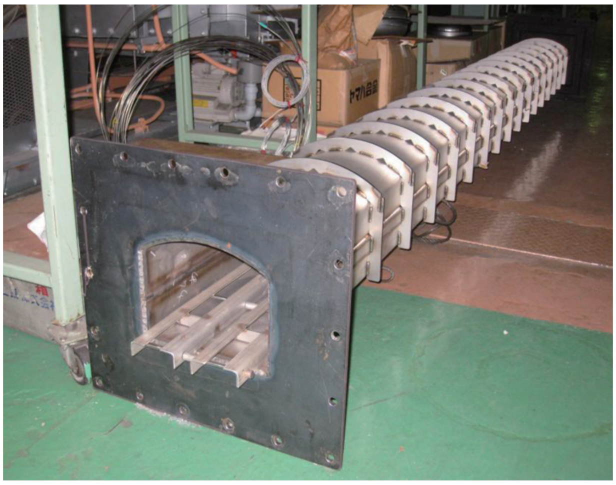

Photo 3 Example of industrial furnace application (muffle furnace Kanto Yakin Kogyo Co., LTD.)

Photo 4 Inside of the gasified melting furnace after working for 2 months

the superheater tube protectors of pulverized-coal-fired boilers and circulation-fluidized-bed (CFB) boilers.

(2) Waste incinerators

AH-4 is effectively applied also for the incineration facilities dealing with municipal and industrial waste. Protectors are provided for the superheater tubes of stoker type boilers for municipal waste incineration, to prevent them from corroding and eroding at working temperatures: AH-4 is used as the material for the protectors due to its excellent erosion resistance. Its applications are also expanding to superheater protectors for biomass-burning boilers. Gasification melting furnaces impose very tough conditions on structural materials because their insides contain a very hot and oxidizing atmosphere. AH-4 is used for the anchors to prevent furnace inner wall refractory linings from falling off. **Photo 4** shows a part of such a wall after operation for two months. Compared with anchors made with SUS 310S, anchors made with AH-4 suffered less thickness loss and were found to hold the lining more effectively. Actually, the need for lining repair decreased significantly.

(3) Cement plants

In the cement production process the raw material is preheated in cyclone heaters where, in addition to being preheated, it is classified according to grain size. For this reason, it is important that the heaters maintain their cyclone shape, which means that, similar to the case of PFBC boilers, high-temperature erosion resistance is essential. The erosion resistance of AH-4 was tested: test pieces of AH-4, each 12 mm thickness × 100 mm × 100 mm in size, were welded onto the inner surface of a cyclone heater inner tube made of SUS 310S, and the heater was put into operation for 10 months. **Figure 9** shows the result: AH-4 wear was only about one-third that of SUS 310S, presumably because of the stable protective oxide films on the surfaces, and the higher strength. In consideration of the test results, use of AH-4 for the entire heater inner tube is being studied.

3.3.3 Automobile parts

(1) Exhaust manifolds

The catalyst for cleaning exhaust gas from automobile engines works efficiently only when it is heated by the gas to within a certain temperature range, and for this reason it is important to heat it quickly to the working temperature after a cold start. Since exhaust gases reach the catalyst converter through exhaust manifolds, decreasing the thermal capacity of the manifolds is effective in shortening catalyst heating time. To decrease thermal capacity, some models have exhaust manifolds with a double-tube structure. The outer tubes are made of thin sheets of ferritic stainless steel having a small thermal expansion coefficient and excellent heat cycle fatigue properties, and the inner tubes, made of austenitic stainless steel with excellent high-temperature strength, are also formed from thin sheets. AH-4 has excellent high-temperature properties, and is used for the inner tubes. To decrease the wall thickness of the inner tubes, it is of special importance that the steel material have high strength, sufficiently high fatigue strength to withstand high-cycle engine vibrations, and resistance to oxidation from the exhaust gases, all at high temperatures.

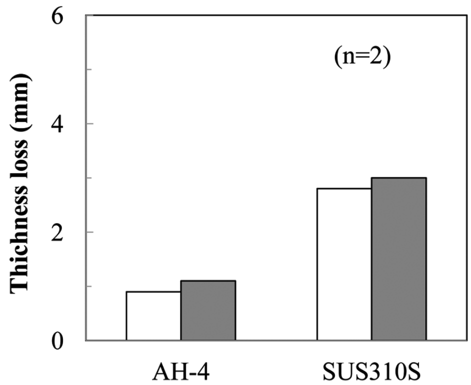

Fig. 9 Comparison of erosion in cement plant (10 months)

Figure 10 compares AH-4 with SUS XM15J1 (the latter being conventionally used for exhaust manifold inner tubes), in terms of tensile properties (0.2% proof stress and tensile strength) at 800°C. As seen here, the high-temperature tensile properties of AH-4 are higher than those of SUS XM15J1, by 40% or more. **Figure 11** shows the results of high-temperature, high-cycle fatigue tests. The inner tubes of double-tube manifolds are hot and vibrating during operation. According to the results of automobile engine durability tests, the cause of inner tube failure is mostly fatigue due to high-cycle vibrations at high temperatures. Resistance to this type of fatigue is therefore most important for the inner tube material. In addition to high-temperature strength, AH-4 also has excellent fatigue

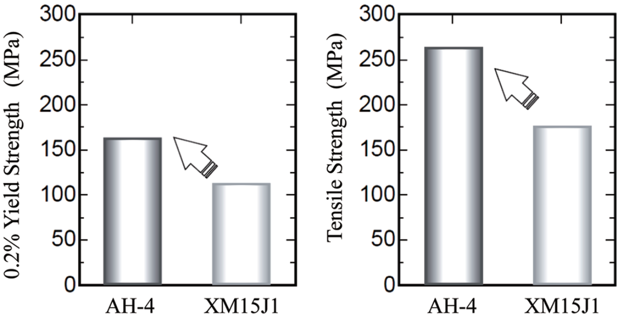

Fig. 10 Tensile properties of AH-4 and SUS XM15J1 at 800˚C

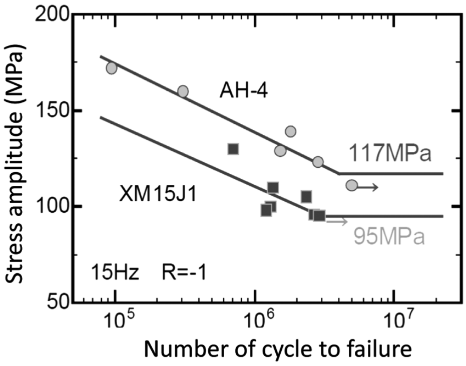

Fig. 11 S-N plots of AH-4 and SUS XM15J1 at 800˚C

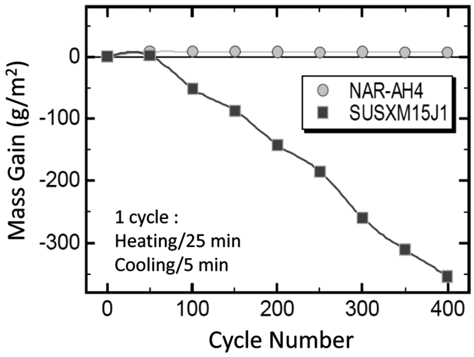

Fig. 12 Cyclic oxidation properties of AH-4 and SUS XM15J1 at 1,000˚C

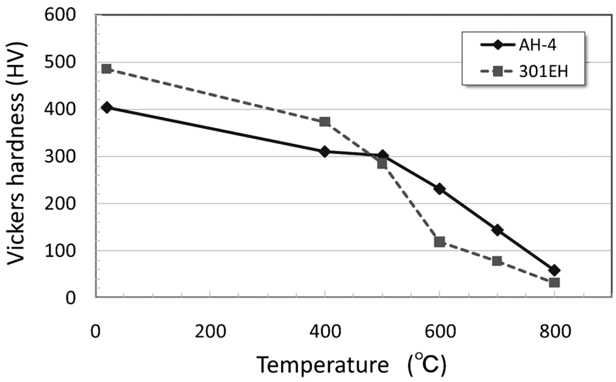

Fig. 13 Vickers hardness of AH-4 and SUS 301EH at high temperature

properties protecting against high-cycle vibrations at high temperatures; its fatigue limit at 800˚C is higher than that of SUS XM15J1, by 20% or more.

Figure 12 shows the results of cyclic oxidation tests at 1,000˚C. Since automobiles typically stop and start fairly often, exhaust manifolds must have good oxidation resistance to withstand repeated heating and cooling cycles (heat shock). With SUS XM15J1, the oxidation resistance of which is improved by Si addition, oxide films gradually flaked off after cycles of heat shock, experiencing a weight loss. In contrast, with AH-4, to which rare-earth metals are added so that tightly packed and highly adhesive protective oxide films form on the surface, no substantial weight loss was recorded. Owing to these properties, AH-4 makes it possible to decrease the wall thickness of exhaust manifolds, which has proved to be effective in enhancing the cleanness of exhaust gas.[3, 4)]

(2) Turbochargers

One of the latest trends in auto engine design is supercharged downsizing, where a turbocharger is provided and engine displacement is reduced to enhance fuel efficiency without sacrificing travelling performance. Since turbochargers are driven by high-temperature exhaust gases from the engine, they are made of materials excellent in heat resistance. According to the latest engine design philosophy aiming to enhance fuel efficiency especially through turbocharger use, lean combustion assisted by a high supercharging ratio is envisaged, and as a result, exhaust gas temperatures would tend to be high. This motivates the search for materials having a heat resistance superior to conventional ones, such as SUS 310S and SUS XM15J1. With its excellent high-temperature properties and cost performance, AH-4 is considered promising, and its application for turbochargers is being studied.

(3) Exhaust gaskets

Sealing materials (exhaust gaskets) are provided at the joints of exhaust gas systems to prevent gases from leaking to the exterior. Thin sheets of metastable austenitic stainless steel, JIS SUS 301 (17%Cr-7%Ni), of the temper grade H or EH according to JIS G 4313 (2011), which have had their strength improved through cold rolling, are widely used for this application. Gas sealing ability is provided by the repulsive force of the steps (called beads) of the sheets formed by presswork. Conventionally, the working temperature of the gaskets used to be 500˚C or less, but exhaust gas temperatures have risen recently owing to the use of turbochargers and other equipment, so gasket working temperatures have risen accordingly. As a result, work-induced martensite, which is responsible for the strength of cold-rolled SUS 301 sheets, transforms back into soft austenite, often leading to a weakening in the repulsive force of the beads.

Because work-induced martensite does not form in AH-4 through cold rolling, and because AH-4 maintains sufficiently high strength at high temperatures without cold rolling (thanks to the solution hardening effects of nitrogen), it is adequate for exhaust gaskets used at high temperatures. **Figure 13** compares the hardness of cold-rolled AH-4 at high temperatures with that of SUS 301EH. Since it is essential for exhaust gaskets to maintain the repulsive force of the beads at high temperatures, high-temperature hardness is of special importance, to prevent softening. Whereas SUS 301EH hardness falls markedly at temperatures above 500˚C, the decrease in the hardness of AH-4 is less than that of the former, demonstrating its superiority. Although AH-4 gradually softens as a result of the recovery and recrystallization of austenite as the temperature rises, work-hardened austenite remains even at 600˚C, maintaining a hardness of 200 HV or higher. This indicates that AH-4 is adequately applicable for exhaust gaskets at temperatures exceeding 500˚C, the temperature at which SUS 301EH becomes too soft.

4. Closing

Nippon Steel & Sumitomo Metal has developed AH series heat-resistant austenitic stainless steel. This paper has focused on AH-4, the most versatile of the AH series steels, and has presented its characteristics and applications.

AH-4 is excellent in oxidation resistance, tensile strength, and creep properties in high-temperature ranges up to 1,000˚C. In addition, it does not embrittle after long use at high temperatures, thanks to its stable metallographic structure; it is resistant to weld cracks, and is also cost efficient because the rational alloy design minimizes Ni content.

Owing to these advantages, this steel is superior to JIS SUS 310S or Alloy 800 when used for structures where deformation resistance at high temperatures is required. It is being applied for heat treatment furnaces and other industrial equipment.

AH-4 has been registered by the American Society for Testing and Materials (ASTM) and the American Society of Mechanical Engineers (ASME), and thus its use outside Japan is expected to expand. Its advantages also include an allowable tensile stress higher than that of SUS 310S, and it gives greater freedom in the design of pressure vessels.

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Shinya YAMAMOTO
Seninor Manager
Specialty Stainless Steel Technical Service &
Solution Dept.
Titanium & Specialty Stainless Steel Unit
2-6-1 Marunouchi, Chiyoda-ku, Tokyo 100-8071

Yoshitaka NISHIYAMA
Chief Researcher, Dr.Eng.
Hydrogen & Energy Materials Research Lab.
Steel Research Laboratories

Yuichi FUKUMURA
Manager
Specialty Stainless Steel Technical Service &
Solution Dept.
Titanium & Specialty Stainless Steel Unit