Development of A New Heat Resistant Austenitic Stainless Steel "NAR-AH-4"

by
Yoshitaka Nishiyama / Research Engineer, Chemical Research Dept., Corporate R&D Lab.
Yoshiatsu Sawaragi / Dr. Eng., Principal Researcher, Corporate R&D Lab.
Takaaki Matsuda / Assistant General Manager, Stainless Steels & Titanium Technology Dept., Head Office
Shigemitsu Kihara / Dr. Eng., General Manager, Material Technology Dept., Research Institute, Ishikawajima-Harima Heavy Industries CO., LTD.
Ichiro Kajigaya / Manager Engineering Group, Basic Design Dept., Power Plant Div., Ishikawajima-Harima Heavy Industries CO., LTD.

Synopsis

New austenitic stainless steel, NAR-AH-4, which consists of LowSi-23mass%Cr-11.5%Ni-0.2%N-B-REM (Rare Earth Metal) has been developed for the application of high temperature components (up to 1000 ℃) in thermal power plants and chemical plants.

The corrosion and erosion resistance for developed steel with high content of chromium and slight amount of REM is excellent by forming adherent chromia oxide film on a surface. The creep rupture strength is considerable higher than that of Type 310S (25Cr-20Ni) and Alloy 800H (20Cr-32Ni-Al,Ti) due to the addition of nitrogen and boron. The resistance to weld hot cracking sensitivity for this steel is better than that for Type 310S and high silicon content austenitic stainless steels, due to decreasing silicon content (0.3%) and optimum ratio of chromium equivalent to nickel equivalent. In addition, this steel has an economic advantage over Type 310S as well as Alloy 800H.

These results indicate that this steel is expected to be widely utilized as candidate material for high temperature components.

1. Introduction

Recently, there is a strong demand for high efficiency power generation to meet environmental regulations and energy saving requirements. Combined cycle power plant such as Pressurized Fluidized Bed Combustion (PFBC), Integrated Coal Gasification Combined Cycle (IGCC) is one of beneficial coal utilization power plant in the early 21st century as well as Ultra Super Critical (USC) plant[1),2)]. It offers high total efficiency ; low NO_X and SO_X emissions; flexibility in choice of coal type; and compact space requirement. These high efficiency power generation systems require high temperature materials to be used in severe hot corrosion (oxidation and sulphidation) and/or erosion environments. Thus the selection of material presents some important problems. Conventional heat resistant austenitic stainless steels such as AISI type 309, AISI type 310S and Alloy 800H are widely applied to the areas of power plants, chemical plants, industrial furnaces and automobile exhaust systems, but these are inferior in corrosion and mechanical strength above 800℃.

In our work, a new austenitic stainless steel with superior high temperature creep rupture strength to AISI type 310S and Alloy 800H and with excellent corrosion and erosion resistance above 800℃, has been developed for high temperature components, e. g. ducts, cyclone and attachment of thermal power plant [3),4)]. This developed steel was designed to ensure excellent weldability, to stabilize microstructure aging long-term service and to reduce material cost. This paper describes the alloying elements design and the properties of the new austenitic stainless steel, NAR-AH-4.

2. Alloy Design of Developed Austenitic Stainless Steel

Alloy design of new developed steel, NAR-AH-4, are shown in **Fig.1.**

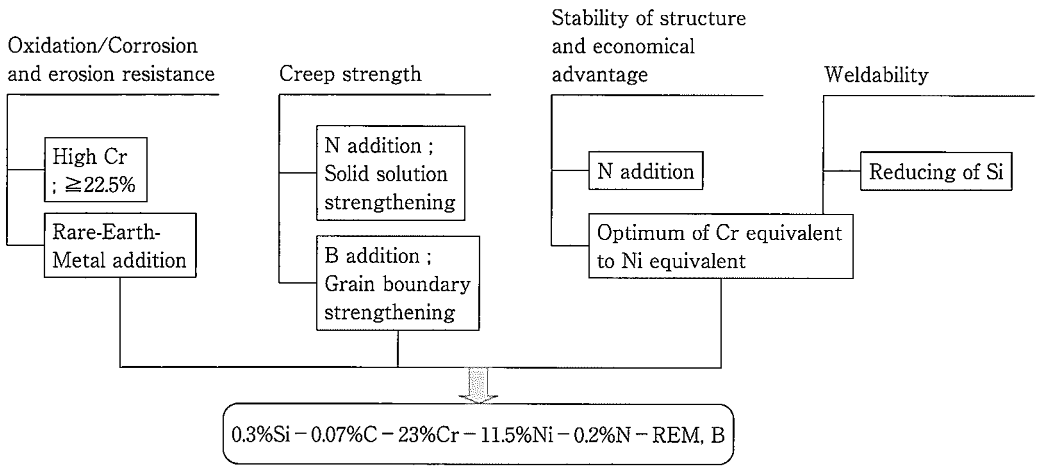


Fig.1 Alloy design of NAR-AH-4

First, high temperature corrosion and erosion resistance are required for using component exposed to severe corrosive gases and / or ash deposits. REM is one of effective elements to improve the corrosion resistance. One of the improvement mechanism proposes that the REM removes sulphur from the scale / matrix boundary, which reduces the adherence of protective oxide film[5),6)]. **Figure 2** shows the effect of cerium content on oxidation resistance of 23Cr-11Ni-0.2N steels. As cerium content increases, the mass gain falls sharply, however, at high cerium levels its effect is small. Thus the optimum value of cerium content is in the range between 0.025 and 0.05mass% and the developed steel contains about 0.03%La+Ce as misch metal. As shown in **Fig.3**, the steel containing 0.03% cerium exhibits particularly excellent oxidation resistance as compared with the steel without cerium under cyclic heating and cooling tests at 900 and 1000℃.

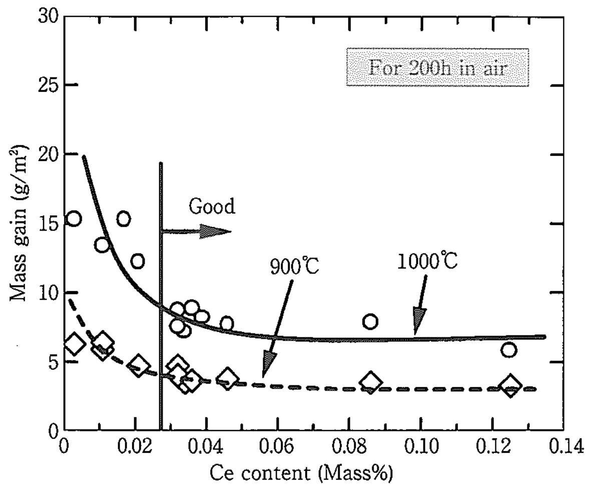
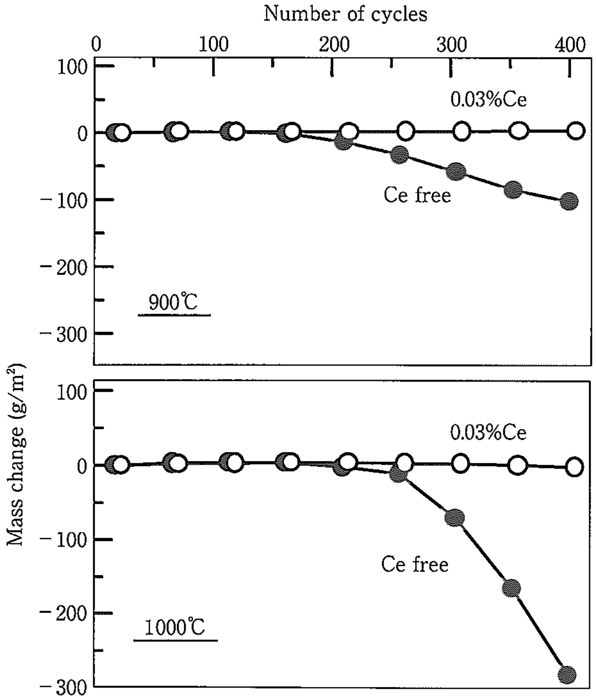


Fig. 2 Effect of Ce content on oxidation resistance of 23Cr-11.5Ni-0.2N steels for 200h in air



(1 cycle : 25min heating-5min cooling)

Fig. 3 Cyclic oxidation resistance of 23Cr-11.5Ni-0.2N steels at 900℃ and 1000℃ in air

Next, high temperature strength is another required property. **Figure 4** shows the effect of nitrogen on rupture time for 26.46MPa×900℃ and 9.8MPa×1000℃. It indicates that time to rupture in-

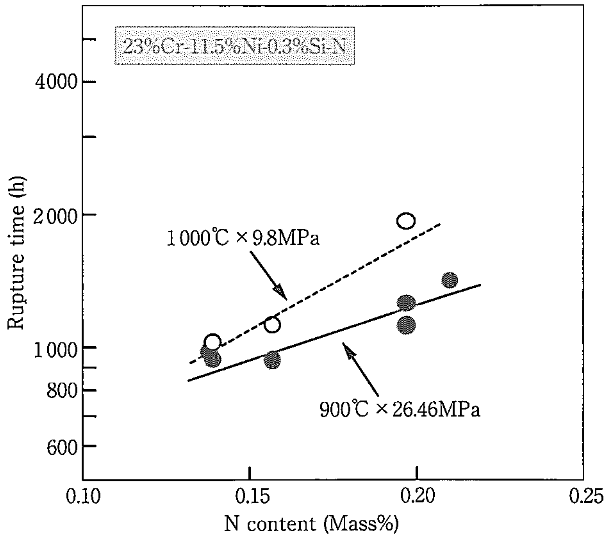


Fig. 4 Effect of N content on rupture strength

creases in proportion to the nitrogen content at both test temperatures. We determined the optimum nitrogen content as 0.2% in consideration of the microstructural phase balance.

Finally, it was designed not to reduce the resistance to weld hot cracking sensitivity. **Figure 5** shows the result of Trans-Varestraint tests with 19-23%Cr-11%Ni-0.2%N containing various levels of silicon. It reveals that silicon is a very harmful element for weld hot cracking sensitivity. Thus the developed steel restricts the silicon content to approximately 0.3%. **Figure 6** shows the effects of nitrogen and nickel on weld hot cracking sensitivity. Nitrogen does not have as much effect up to 0.2%. On the other hand, nickel causes high sensitivity to hot weld cracking due to microstructural phase balance. Therefore, we made an effort to design an optimum ratio of chromium equivalent to nickel equivalent.

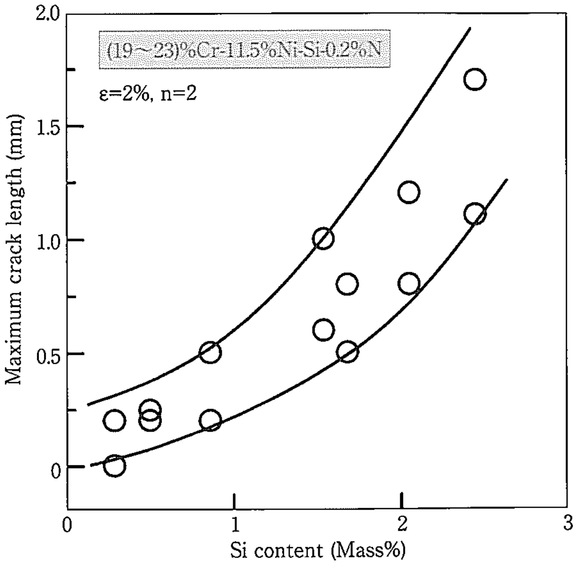


Fig. 5 Effect of Si content on hot cracking sensitivity (Trans-Varestraint test)

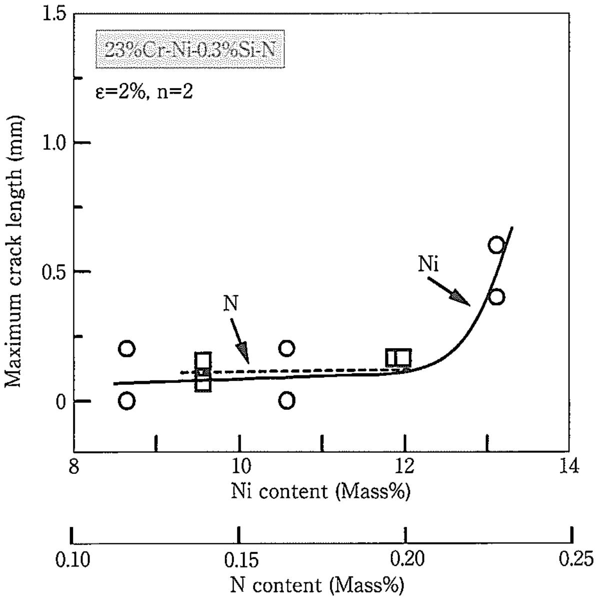


Fig. 6 Effects of Ni and N content on hot cracking sensitivity (Trans-Varestraint test)

3. Characteristic Properties

3.1 Chemical Compositions

Chemical compositions of NAR-AH-4 and some commercial base steels are given in **Table 1**.

NAR-AH-4 was melted by blast furnace or electric arc furnace and refined by a VOD (Vacuum Oxygen Decarburization) process. Then it was solidified into a slab, billet and bloom in the CC (Continuous Casting) machine. NAR-AH-4 can be easily produced on workability. Solution heat treatment may be carried out at 1080 to 1160℃ for appropriate time, water quenched or air cooled. It is available to the hot-rolled plate,

Table 1 Chemical compositions of tested steels (Mass%)

Steels	C	Si	Mn	Cr	Ni	N	Others
NAR-AH-4	0.07	0.36	0.55	23.0	11.2	0.20	0.032La+Ce, 32ppmB
(Spec.)	0.05 /0.10	1.00 Max.	1.00 Max	22.0 /24.0	10.0 /12.0	0.18 /0.25	0.03/0.07La+Ce
AISI type 310S	0.05	0.6	1.2	24.6	20.2		–
Alloy 800H	0.07	0.5	0.9	21.0	32.4		Ti, Al
ASTM UNS S30815	0.07	1.4	0.7	21.0	10.8	0.17	REM
SUS XM15J1	0.06	3.4	0.7	19.0	12.8		
AISI type 304	0.07	0.6	0.7	18.2	8.2		

cold-rolled sheet and coil, seamless tube and welded pipe and in addition bar, wire and forgings products on request.

3.2 Mechanical Properties

Tensile properties, hardness and toughness at room temperature are shown in **Table 2**. These properties are satisfied with specifications.

Table 2 Tensile properties, hardness and toughness of NAR-AH-4 at room temperature

	Short-tensile*			Hardness	Charpy impact**
Specimen	Yield strength (MPa)	Tensile strength (MPa)	Elongation (%)	HRB	V_E (J/cm^2)
Sheet (20^{t}mm)	309	690	60	86	250.5
Spec.	≧280	≧600	≧40	≦95	–

*JIS No.14A (ϕ6mm) ; L-direction
**5 × 10mm (2mm V-notch) ; T-direction

3.3 High Temperature Corrosion and Erosion

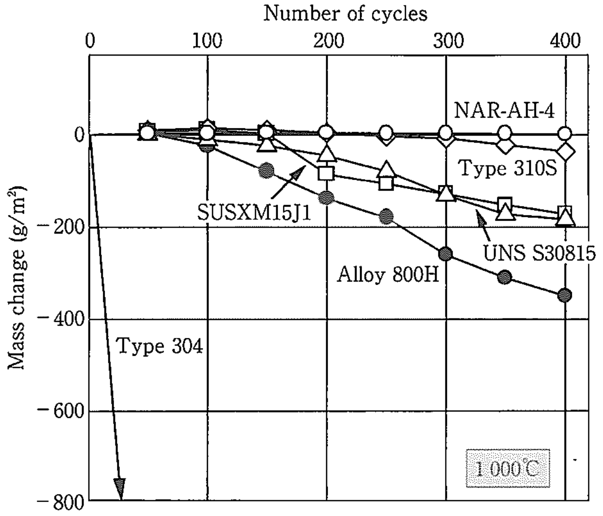
The results of isothermal heating test at 900 to 1100℃ for 200h in air are listed in **Table 3**. This indicates mass gain of NAR-AH-4 is equal to that of ASTM UNS S30815 and SUS XM15J1 which contain high silicon, and is much better than that of Type 310S, Alloy 800H and Type 304.

Table 3 Mass gain of some steels for isothermal heating test at 900-1000℃ for 200h in air

Mass gain (g/m^2)

Tested temp. (℃)	NAR-AH-4	Type 310S	Alloy 800H	UNS S30815	SUS XM15J1	Type 304
900	5.1	8.2	8.5	6.0	4.0	14.6
1000	12.4	20.7	22.1	13.3	12.0	>150
1050	22.4	31.0	42.6	21.2	20.8	–
1100	41.3	39.2	59.8	31.8	30.9	–

Figure 7 shows mass change of some steels conducted by the cyclic heating test at 1000℃ in air. Tests were executed up to 400cycles, which were done on 25min. heating and 5min. air-cooling cycle. NAR-AH-4 exhibits excellent oxidation resistance under conditions of severe thermal changes. This means protective chromia oxide film formed on the surface is maintained during long-term exposure due to its relatively high chromium content and addition of REM. High silicon content steels, UNS S30815 and SUS XM15J1, which exhibit excellent oxidation resistance in continuous heating tests, are inferior in cyclic oxidation resistance. This would suggest that silicon oxide is protective against diffusion of cation / anion, but it diminishes the adherence of scale and base metal with thermal stress because thermal coefficient expansion of silicon oxide is considerably difference from that of austenitic structure.



(1 cycle is 25min heating-5min air cooling)

Fig. 7 Results of cyclic oxidation test performed up to 400 cycles at 1000℃

Figure 8 shows the results of erosion tests performed at 900℃ up to 100hrs. Tests was conducted in fluidized erodent, KASHIMA sand, mainly contents of 85.5% silica and 4% alumina at a velocity of 5m/sec. Test pieces are column shaped, 15mm in diameter and 40mm in length. After testing for 100h, mass loss and maximum depth of thickness loss of

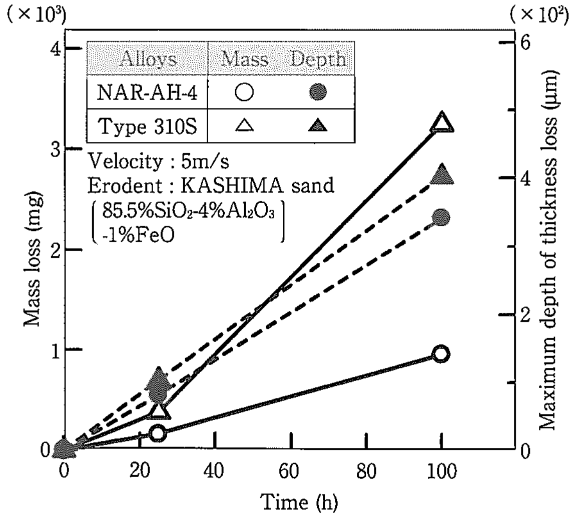


Fig. 8 Result of fluidized bed type erosion tests performed at 900℃ up to 100h

NAR-AH-4 are less than that of Type 310S. These results confirm that erosion resistance of NAR-AH-4 are superior to that of Type 310S due to form adherence chromia oxide film on surface..

3.4 Creep Rupture Properties

Figure 9 shows the results of creep rupture tests of NAR-AH-4 at 800 to 1000℃. Considerable data have been collected and some tests at 30000h are still in progress. It proved that the creep rupture properties of steels prepared with nitrogen additions, boron addition and coarse grain size, are very stable. A rapid decrease of the rupture strength has not been recognized in the region of high temperature over 800℃. **Figure 10** shows the comparison of stress to rupture at 10000h for various alloys. This indicates NAR-AH-4 is superior to other alloys between all the range of test temperature. **Table 4** shows the creep rupture strength of this steel at each temperature.

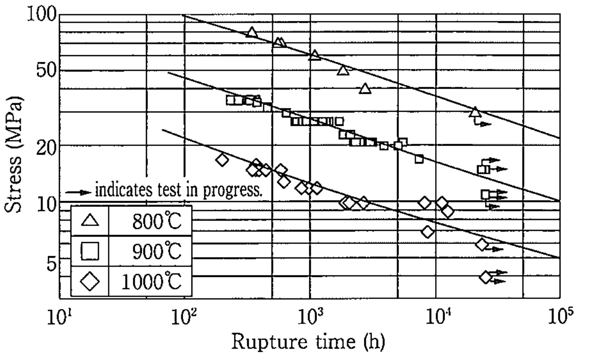


Fig. 9 · Stress-rupture plot of developed steels at 800-1000℃

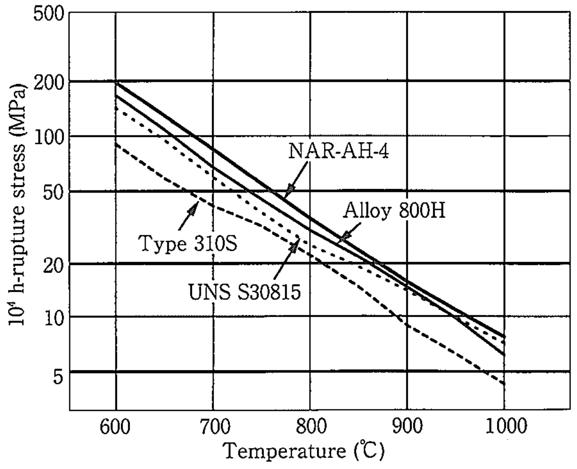


Fig. 10 Comparison of stress to give ruputure at 10^4h for various alloys

Table 4 Creep rupture strength of NAR-AH-4 at 600-950℃

(MPa)

Rupture time (h)	Temp. (℃)							
	600	650	700	750	800	850	900	950
10000	201.9	128.4	83.3	53.9	35.3	23.62	15.88	10.78
100000	132.3	83.3	52.9	34.3	22.5	14.60	9.70	6.47

3.5 Properties and Microstructural Observation after Aging

It is important to clarify the properties of the materials during long-term exposure at high temperature. Charpy impact test at 20℃ aged for 3000hrs at 700 to 900℃ are shown in **Fig.11**. Impact value of NAR-AH-4 is more than 60J/cm², which is superior to that of Type 310S at all test temperatures.

Identification of these precipitation was conducted by extracted residue and X-ray analysis. The main precipitate which appears on aging at 700 to 900℃ is $M_{23}C_6$ (M=Fe, Cr) carbides. No brittle compounds such as sigma phase detected in Type 310S and phai phase detected in high nitrogen and silicon content steels have been identified[7].

Optical microstructure after aging for 300h and 3000h at 700 to 900℃ are shown in **Photo 1**. It revealed only fine precipitates with length of 0.5-1μm at grain boundaries and in the matrix. Thus it is concluded that NAR-AH-4 has high microstructural phase stability and toughness, even after a long time at high temperature.

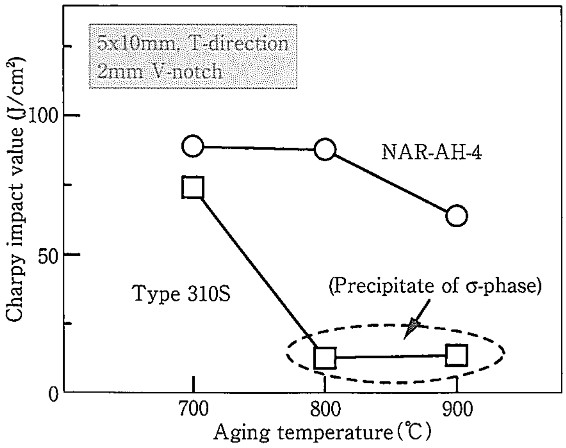


Fig. 11 Charpy impact properties at 20℃ after aged for 3000h

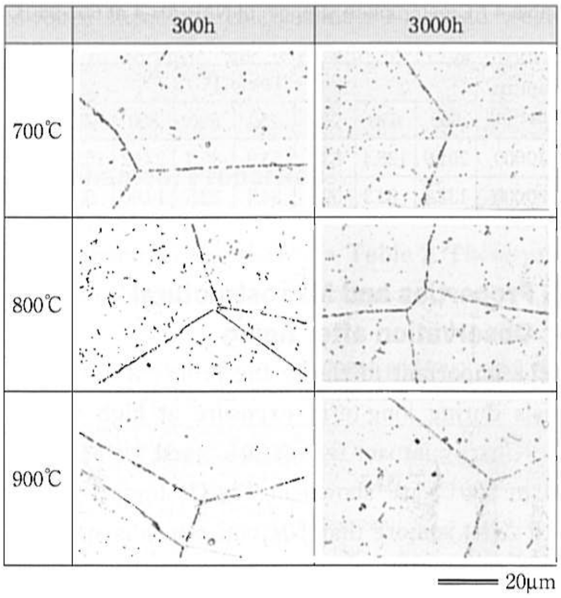


Photo 1 Microstructure after long aging at 700,800 and 900℃

3.6 Weldability

Weldability of NAR-AH-4 was evaluated by the hot cracking sensitivity test and welded joint test. Trans-Varestraint test and restrained test to clarify the hot cracking sensitivity were examined as shown in **Fig.12(a)(b)**. These results show that hot crack sensitivity of this steel is much better than that of Type 310S.

Gas shielded TIG and MIG wire and coated electrodes of NAR-AH-4 are already developed. These electrodes are with the same compositions of base metals containing additional molybdenum to improve the strength at joint. Chemical compositions of gas shielded TIG wire are shown in **Table 5**. Creep rupture properties of welded joints are shown in **Fig.13**. Specimens of 6mm in diameter were welded by TIG and coated electrodes. The creep rupture strength level of welded joints lies within the data band of base metal.

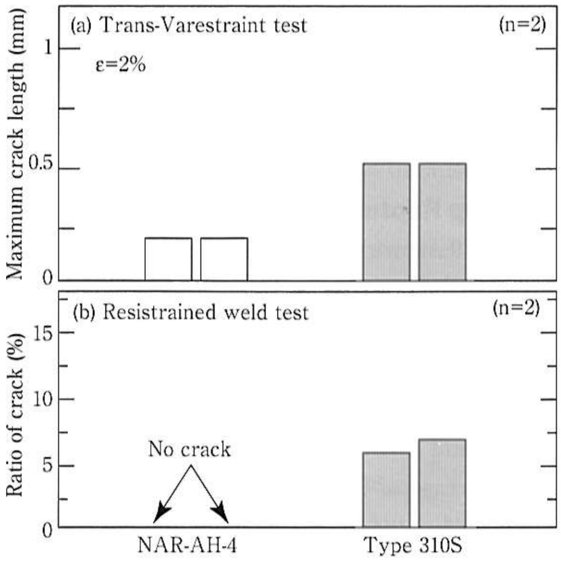


Fig. 12 Hot cracking test result
(a) Trans-Varestraint test
(b) Resistrained weld test

Table 5 Chemical compositions of gas shielded TIG wire (Mass%)

C	Si	Mn	Cr	Ni	Mo	N	Others
0.06	0.31	0.53	22.7	12.2	1.00	0.26	REM, B

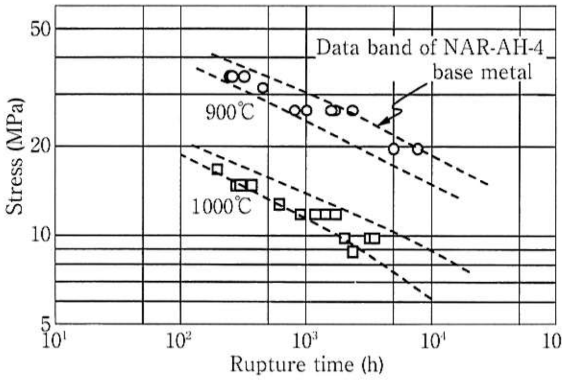


Fig. 13 Creep rupture properties of welded joints

4. Conclusions

The corrosion and erosion resistance for developed steel with high content of chromium and slight amount of REM is superior to that of AISI type 310S and Alloy 800H. Especially NAR-AH-4 exhibits an excellent oxidation resistance up to 1000℃ due to the formation of protective chromium oxide film.

The creep rupture strength is considerable higher than that of AISI type 310S and Alloy 800H and high silicon, nitrogen-containing steel due to the addition of nitrogen and boron. The microstructural stability of NAR-AH-4 is superior to that of AISI 310S. The main precipitates at grain boundary and in the matrix of NAR-AH-4 after long-term aging are $M_{23}C_6$ carbides. Brittle compounds such as sigma and phai phase are not observed.

The resistance to weld hot cracking sensitivity for this steel is better than that of AISI type 310S and high silicon content austenitic stainless steels, due to decreasing silicon content (0.3%) and optimum ratio of chromium equivalent to nickel equivalent. The creep rupture strength level of welded joints lies within the data band of base metal.

As described above, the newly developed steel, NAR-AH-4, can be widely utilized as candidate material for high temperature components of thermal power plants, chemical plants, industrial furnaces and automobile exhaust systems.

Yoshitaka Nishiyama

Research Engineer,
Chemical Research Dept.,
Corporate R&D Lab.

Phone: 06(6489)5729

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