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Development of Tubes and Pipes for Ultra-Supercritical Thermal Power Plant Boilers

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Abstract:

In recent years, the steam temperature and pressure of thermal power plant boilers have been raised to the supercritical levels of 246 atm and 566°C, respectively, for better energy efficiency. More lately, the prevailing call for the protection of global environment is giving momentum to the world-wide study of technology to further enhance the efficiency of thermal power generation. The immediate targets of boiler steam pressure and temperature are 316 atm and 593°C, while the ultimate targets are 352 atm and 649°C. After extensive research made into steel tubes and pipes capable of withstanding these ultra-supercritical steam conditions, Nippon Steel developed a 9Cr-0.5Mo-1.8W-Nb-V ferritic steel and a 20Cr-25Ni-1.5Mo-Nb-Ti-N austenitic steel for ultra-supercritical applications. The former steel has 600°C creep rupture strength that is equal to or higher than that of the 18-8 austenitic stainless steel. The latter steel has far higher elevated-temperature corrosion resistance than the conventional 17-14CuMo steel, and features 700°C × 10^5 h creep rupture strength of 88 MPa, a value which is equal to or higher than that of the 17-14CuMo steel.

1. Introduction

In recent years, the demand for improving the efficiency of thermal power plants from an energy-saving point of view has raised the boiler steam pressure and temperature to the supercritical levels of about 246 atm and 566°C, respectively. More recently, measures for further enhancing the efficiency of thermal power generation have come to be extensively studied throughout the world for the protection of the global environment. The target values of boiler steam conditions are 316 atm and 593°C in the short run and 352 atm and 649°C in the long run[1].

The development of materials that can withstand such high

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steam pressures and temperatures is indispensable for realizing ultra-supercritical thermal power plants. After extensive research into steel tubes and pipes capable of withstanding the ultra-supercritical steam conditions, Nippon Steel developed a 9Cr-0.5Mo-1.8W-Nb-V ferritic steel, designated NF616, and a 20Cr-25Ni-1.5Mo-Nb-Ti-N austenitic steel, designated NF709, for ultra-supercritical applications. The allowable temperature of the new steels at the allowable tensile stress of 49 MPa is compared with that of conventional steels in **Fig. 1**[2]. NF616 is a high-strength ferritic grade with its 600°C creep rupture strength far exceeding that of the modified 9Cr-1Mo ferritic steel T91 developed in the United States, being equal to or higher than that of the 18-8 austenitic stainless steel. NF709 is a high-strength and high-corrosion resistance austenitic steel with 700°C creep rupture strength equal to or higher than that of the 17-14CuMo steel and elevated-temperature corrosion resistance much higher than that of the 17-14CuMo steel.

The development of the two new steels for ultra-supercritical boiler tubes and pipes is reported here.

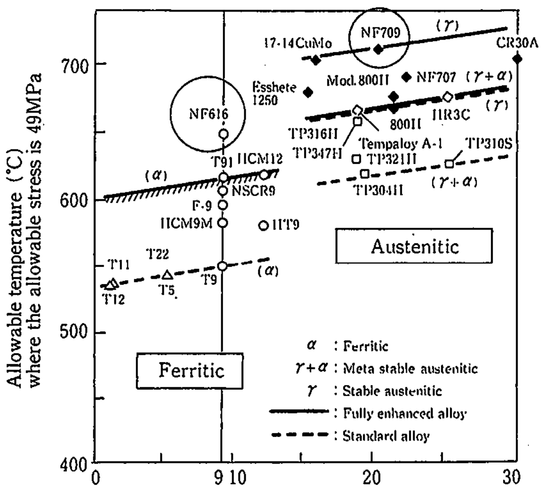


Fig. 1 Comparison of new steels with conventional steels in heat resistance (excerpted from Masuyama[2] and partly augmented)

Table 1 Chemical compositions of NF616 steels tested (mass %)

Heat	C	Si	Mn	Cr	Mo	W	V	Nb	N
A	0.070	0.06	0.42	8.98	0.52	1.65	0.16	0.049	0.038
C	0.085	0.06	0.45	9.00	0.50	1.80	0.20	0.054	0.048
D	0.088	0.06	0.45	9.01	0.50	1.77	0.20	0.054	0.048
E	0.10	0.10	0.47	9.05	0.49	1.72	0.21	0.060	0.037

2. Development of 9Cr-0.5Mo-1.8W-Nb-V Ferritic Steel NF616 for Boiler Tubes and Pipes

2.1 Manufacture and elevated-temperature properties of boiler tubes

2.1.1 Test methods

(1) Test materials

The chemical composition[3] of the test material is the same as that of the 9Cr-2Mo steel except that some of the molybdenum is replaced by tungsten to obtain solid-solution strengthening with 0.5% Mo and 1.8% W. Vanadium and niobium are added to ensure precipitation strengthening with carbonitrides, and a single phase of tempered martensite without δ-ferrite is aimed at. Three heats were made in a vacuum melting furnace to the chemical compositions listed in **Table 1**. Ingots were forged into round billets and hot extruded into 54.0 mm diameter and 10.6 mm wall tubes for steel A, 52.6 mm diameter and 9.8 mm wall tubes for steel C, and 38.1 mm diameter and 6.0 mm wall tubes for steel D. The tubes were normalized at 1,050°C and tempered at 775°C from considerations of creep rupture strength, tensile strength, and toughness. The modified 9Cr-1Mo steel was made as control.

(2) Test conditions

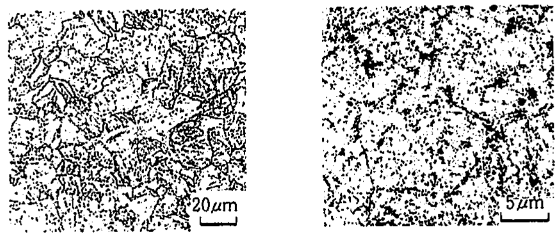
The tubes were examined macroscopically and microscopically, and tested for tensile properties at room temperature to 800°C, for creep rupture strength at 600, 650 and 700°C and for toughness after aging at 600 and 650°C for 1 to 10^4 h. To investigate weldability, a piece was machined from each bloom, rolled into a 15-mm thick plate, and tested for weld cracking. The plates were also TIG welded using a newly developed matching filler metal. The TIG welded joints were heat treated at 740°C for 1 h and then creep rupture tested.

2.1.2 Test results and discussion

(1) Mechanical properties

Photo 1 shows the microstructure and precipitates of steel D. The microstructure is composed of a single phase of tempered martensite. No δ-ferrite is observed, and precipitate particles are finely dispersed. The tensile strength and yield strength at 500°C and lower are approximately the same as those of the modified 9Cr-1Mo steel, but are higher at higher temperatures, probably due to solid-solution strengthening by the tungsten addition.

(2) Long-term elevated-temperature properties



Microstructure Precipitates

Photo 1 Microstructure and precipitates of NF616 (steel D)

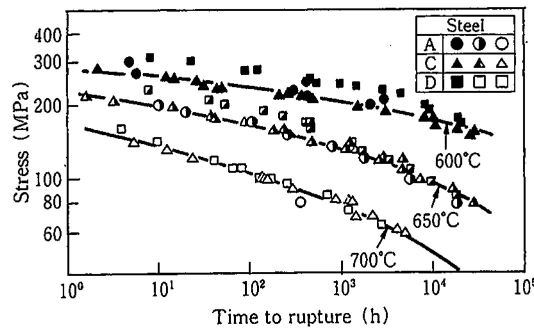


Fig. 2 Stress-creep rupture time curves of NF616 (steels A, C and D)

Fig. 2 shows the stress-creep rupture time curves of steels A, C, and D. The curves mildly slope and indicate stable long-term creep rupture properties at maximum time data of about 30,000 hours. When arranged and estimated by the Larson-Miller parameter (LMP), the creep rupture stress at 600°C in 10^5 h is 142 MPa. This value is much higher than that of the existing 9Cr-1Mo ferritic steel and is equal to or higher than that of austenitic stainless steels.

The impact test results of steel D after aging are shown in **Fig. 3**. Toughness decreases by aging, but stabilizes after 3,000 h and over. Toughness after aging at 600°C for 10^4 h is 64 J/cm^2; which is high enough for boiler tubes. **Table 2** shows the changes in the precipitates of steel D with aging temperature and time. Nb(C, N) and $M_{23}C_6$ precipitate in the as tempered condition. At 600°C, 1,000-h aging starts M_6C and Laves phase precipitation in large amounts. The precipitates are agglomerated at prior austenite grain boundaries and martensite lath boundaries, but no marked coarsening is observed in the long term.

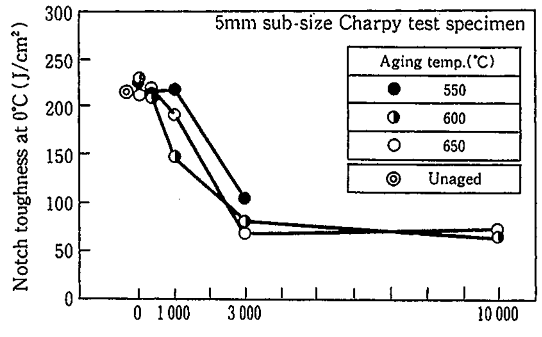


Fig. 3 As-aged toughness of NF616 (steel D)

Table 2 Change in precipitates in NF616 (steel D) as examined by X-ray diffraction

Time / Temp.	1h	10h	10^2h	10^3h	3×10^3h	10^4h
550°C	Nb (C, N) $M_{23}C_6$ M_6C	Nb (C,N) $M_{12}C_6$ M_6C	Nb (C, N) $M_{12}C_6$ M_6C	Nb (C, N) $M_{12}C_6$ M_6C	Nb (C, N) $M_{12}C_6$ M_6C	
600°C	Nb (C, N) $M_{23}C_6$	Nb (C, N) $M_{23}C_6$	Nb (C, N) $M_{23}C_6$ M_6C	Nb (C, N) $M_{23}C_6$ M_6C Laves	Nb (C, N) $M_{12}C_6$ M_6C Laves	Nb (C, N) $M_{23}C_6$ M_6C Laves
650°C	Nb (C, N) $M_{23}C_6$	Nb (C, N) $M_{23}C_6$	Nb (C, N) $M_{23}C_6$	Nb (C, N) $M_{23}C_6$ M_6C Laves	Nb (C, N) $M_{23}C_6$ M_6C Laves	Nb (C, N) $M_{23}C_6$ M_6C Laves

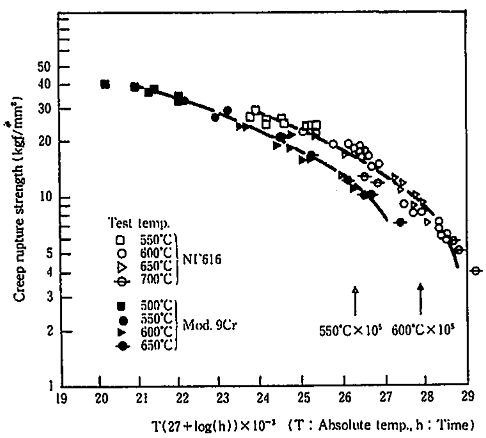


Fig. 4 Creep rupture properties of TIG welded joints of NF616

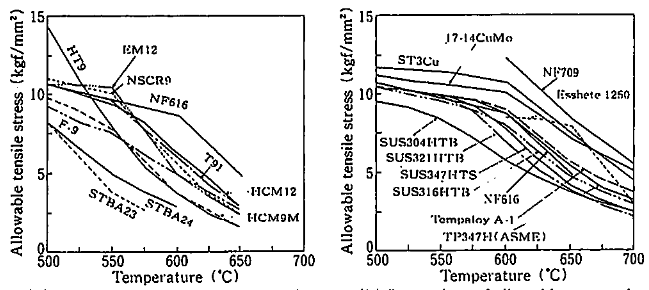
(3) Weld properties

In small y-groove weld cracking test, weld cracking is arrested by 100°C pre-heating, and weld cracking sensitivity is low. In **Fig. 4**, the creep rupture strength of TIG welded joints of NF616 is compared with that of the modified 9Cr-1Mo steel by the Larson-Miller parameter. The creep rupture strength of the weld metal is somewhat lower than that of the base metal, but is much better than that of welded joints of the modified 9Cr-1Mo steel.

2.2 Application of tubes in actual boiler

2.2.1 Calculation of allowable tensile stress

The allowable tensile stress of the NF616 steel is calculated according to the criteria of the Ministry of International Trade and Industry, and is compared in **Fig. 5** with that of 9 to 12Cr ferritic steels and austenitic stainless steels. As indicated, the allowable tensile stress of NF616 over the temperature range of 500 to 650°C is far better than those of T91, SUS304HTB and SUS347HTB.



(a) Comparison of allowable stresses for 9~12% Cr steels
(b) Comparison of allowable stresses for 18Cr-8Ni steels and 15Cr-15Ni steels

Fig. 5 Allowable tensile stress of NF616 and NF709 (excerpted from Masuyama[2]) and partly augmented)

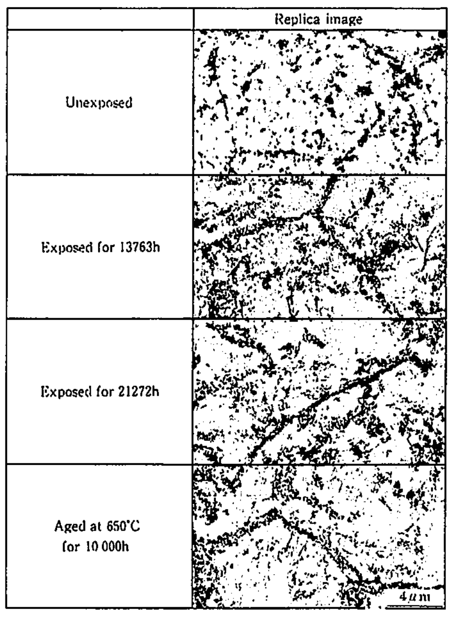


Photo 2 Change in morphology of precipitates in NF616 (steel D) in boiler test

2.2.2 Boiler test

Authorized by the Ministry of International Trade and Industry, NF616 steel tubes have been under test in No. 4 boiler at the Tobata Thermal Power Plant of Tobata Cooperative Thermal Power Plant Co., Ltd. since 1987. The boiler features a maximum operating pressure of 19.3 MPa, maximum operating temperature of 569°C and metal temperature of 600°C, and is fired by blast-furnace gas and other fuels. The test tubes were made of steel D. At the factory, 300-mm long tubes were joined into a 600-mm long tube by TIG welding with a matching filler metal. A SUS321H tube was attached to each end of the 600-mm long NF616 steel tube to form a 1-m tube by dissimilar metal welding. The test tubes were installed to take the place of the SUS321H steel tubes in the uppermost high-temperature section of the tertiary superheater of the boiler. The first and second test tubes were removed from the boiler at 13,673 and 21,272 h, respectively, after the start of the boiler test.

Photo 2 shows the change in the morphology of precipitate particles observed in the two removed test tubes as compared with an unexposed tube and a tube aged at 650°C for 10^4 h (this heat treatment corresponds to aging at 600°C for about 2×10^6 h). The precipitate particles in the removed tubes coalesce but not coarsen as compared with the unexposed tube. The two removed tubes are practically the same as the 650°C × 10^4 h aged tube in the precipitate morphology. These results confirmed the stability of quality in the NF616 steel after long-time aging.

2.3 Manufacture and elevated-temperature properties of boiler pipes

2.3.1 Test methods

(1) Test materials

Steel E was made in a vacuum melting furnace to the chemical composition shown in Table 1. The ingot was forged into a 290-mm square billet and formed into 352 mm diameter and 56 mm wall pipe at a seamless pipe mill. The pipe was normalized at 1,065°C and tempered at 760°C.

(2) Test conditions

Specimens were machined from the pipe in the longitudinal (L), circumferential (C), and thickness (Z) directions. They were examined macroscopically and microscopically, and were put to tensile tests at room temperature to 700°C, creep rupture tests at 550, 600, 650 and 700°C, and impact tests after aging at 600°C for 100 to 3,000 h. A piece was machined from the bloom, rolled into a 50-mm thick plate, submerged arc welded, and tested for creep rupture strength.

2.3.2 Test results and discussion

(1) Elevated-temperature properties of base metal

The microstructure is tempered martensite containing less than 1% of δ-ferrite. Precipitate particles are finely dispersed. The tensile test results are almost the same as those of the tubes.

Fig. 6 shows the 600°C creep rupture test results as compared with the modified 9Cr-1Mo steel and Europe's typical 12Cr steel X20. The slope of the curve for NF616 is gentler than for the other steels, and this difference of gradient increases with increasing time. The NF616 steel exhibits no significant difference between the L, C, and Z directions. When the pipe and tube are compared in creep rupture properties, the creep rupture strength of the pipe is lower than that of the tubes at the low end of the time range and becomes approximately equal to that of the tubes at the high end of the time range.

The 20°C toughness of the pipe is 200 J/cm^2 in the heat-treated condition, falls to 50 J/cm^2 after 3,000-h aging, but is still high enough for boiler pipe steel.

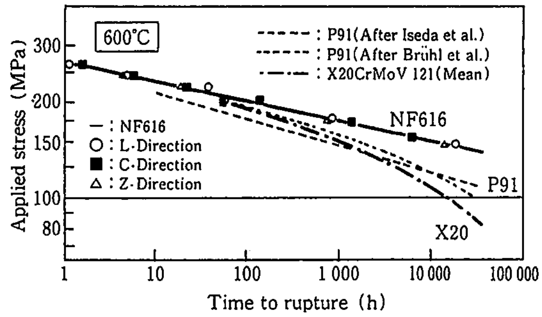


Fig. 6 Stress-creep rupture time curves of NF616 (steel E)

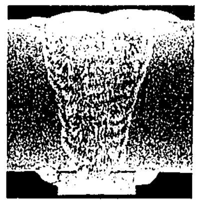


Photo 3 Macrostructure of SAW welded joint of NF616

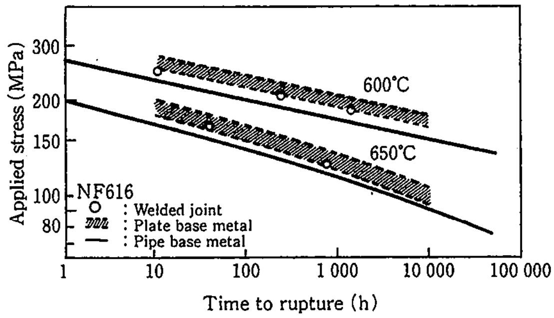


Fig. 7 Creep rupture properties of SAW welded joints of NF616

(2) Elevated-temperature properties of weld metal

The macrostructure of a submerged arc welded (SAW) joint of NF616 is shown in **Photo 3**. A small amount of δ-ferrite is observed near the fusion line. **Fig. 7** shows the creep rupture properties of SAW welded joints as compared with those of steel E pipes and plates. The creep rupture properties of the SAW welded joints are under the lower limits of the plate data, but are above the pipe data.

2.4 Application of pipes in actual boiler

The research of ultra-supercritical boilers is led by the Electric Power Research Institute (EPRI) of the United States and the research association COST of Europe. One of the main technical issues is that as the headers and main steam pipes increase in wall thickness, they are subjected to excessive cyclic thermal stress and are liable to fatigue failure when the boiler is run for load adjustment[4]. This situation has led to demand for the development of ferritic steel pipes with a low thermal expansion coefficient, good thermal conductivity, and high creep rupture strength. NF616 thick-walled pipes have been jointly studied internationally by the United States, Britain, Denmark and Japan[5]. Preparations are now being made for the boiler test of the NF616 thick-walled pipes. Denmark aims at 350 atm and

600°C for future ultra-supercritical boilers and is carrying out the boiler test and evaluation of NF616[6].

3. Development of 20Cr-25Ni-1.5Mo-Nb-Ti-N Austenitic Steel NF709 for Boiler Tubes

3.1 Manufacture and elevated-temperature properties of tubes

3.1.1 Test methods

(1) Test materials

The chemical composition of the test material features 20% Cr for elevated-temperature corrosion resistance and 25% Ni for preventing σ phase precipitation even after an extended period of service. Niobium and titanium are added for precipitate control[7], and molybdenum and nitrogen are added for solid-solution strengthening. This composition ensures stable properties at elevated temperatures for a long period of service. Boiler tubes were manufactured from steel by electric arc furnace melting, argon oxygen decarburization, continuous casting, hot extrusion, cold drawing, and solution heat treatment. **Table 3** gives the chemical composition of the NF709 steel. Aluminum reduction refining and calcium addition were made to impart high hot workability to billets. The as-cast billets were hot extruded into 47.6 mm diameter and 6.3 mm wall tubes. The 17-14CuMo steel, TP310S steel, and TP347H steel were used for comparison.

Table 3 Chemical composition of NF709 (mass %)

Steel \ Element	C	Ni	Cr	Mo	Nb	Ti	B (Cu)	N
NF709	0.07	24.84	19.65	1.44	0.26	0.04	0.005	0.15
17-14CuMo	0.11	14.50	15.90	2.50	0.43	0.24	(3.1)	0.01
TP347H	0.07	11.30	17.80	—	0.72	—	—	0.01
TP310S	0.06	19.80	24.71	—	—	—	—	0.05

(2) Test conditions

The tubes were examined macroscopically and microscopically, and tested for tensile tensile at room temperature to 800°C, for creep rupture tested at 600, 650, 700, 750 and 800°C and for impact tested after aging at 700°C for up to 3,000 h.

The tubes were molten salt corrosion tested in synthetic ash (1.5 mol·K_2SO_4 + 1.5 mol·Na_2SO_4 + 1.0 mol·Fe_2O_3) under a mixed gas (0.5% SO_2 + 5% O_2 + 15% CO_2 + bal. N_2) to simulate the operating environment of a coal-fired boiler at 700°C for 100 h. After this test, the tubes were measured for weight loss and put to electron probe microanalysis (EPMA).

As for weldability, the tubes were subjected to the Varestraint test to evaluate hot weld cracking susceptibility. They were also TIG welded using a newly developed matching metal wire and tested for creep rupture properties.

3.1.2 Test results and discussion

(1) Long-term elevated-temperature properties

Fig. 8 shows the stress-creep rupture time curves of NF709. Creep rupture data are obtained to a maximum time of about 30,000 hours. All curves are linear at temperatures of 650 to 800°C. The creep rupture strength of NF709 at 700°C in 10^4 h is estimated at 88 MPa by the Larson-Miller parameter, which is higher than that of the 17-14CuMo steel.

The Charpy impact value of NF709 in the solution heat-treated condition and after long-time aging at 700°C decreases with increasing aging time, and becomes constant at 30 to 40 J after

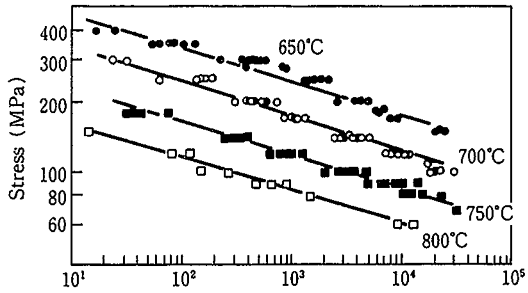


Fig. 8 Stress-creep rupture time curves of NF709

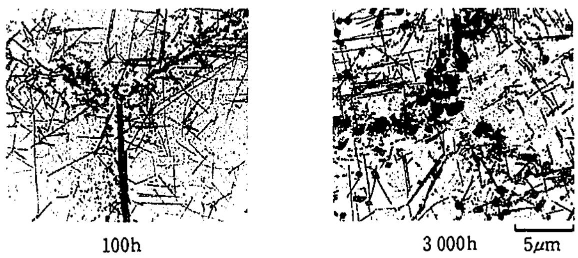


Photo 4 Precipitates in NF709 after aging at 700°C

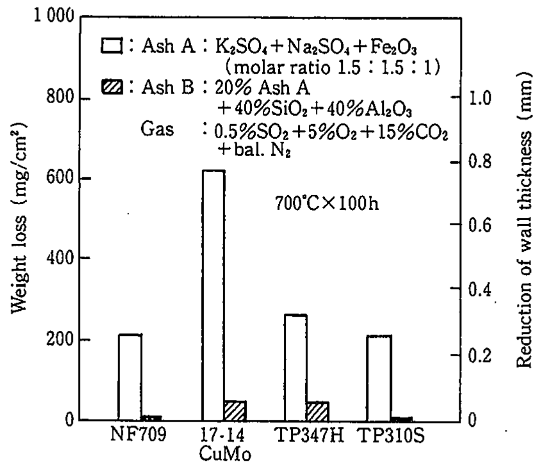


Fig. 9 Corrosion behavior of NF709 in molten salt

more than 1,000 h. The loss of toughness up to 1,000 h is attributable to the precipitation of carbides at grain boundaries and adjacent areas, as shown in **Photo 4**. The toughness is stabilized after 1,000 h, probably because the coarsening of precipitates is retarded and because the precipitation of σ phase is prevented by the balance of nickel and chromium contents even after an extended period of service.

(2) Elevated-temperature corrosion resistance

Fig. 9 shows the weight loss of NF709 determined in molten salt corrosion test by simulating the operating environment of a coal-fired boiler. The elevated-temperature corrosion resistance of NF709 is comparable to that of TP310S containing 23% Cr and is three times as high as that of the 17-14CuMo steel. **Fig. 10** shows the results of EPMA analyses made of the sections of NF709 steel and 17-14CuMo steel specimens after the molten salt corrosion test. NF709 is characterized by a high chromium con-

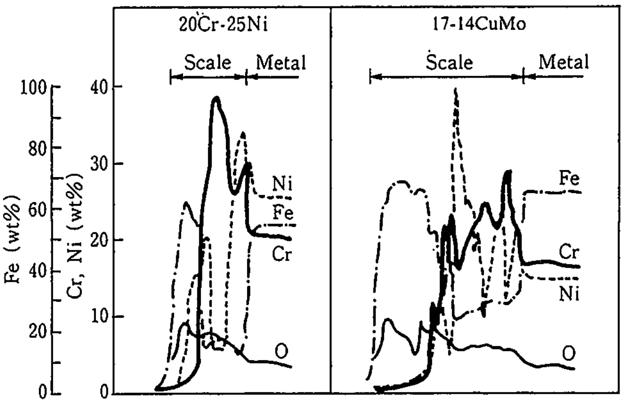


Fig. 10 EPMA analyses of NF709 steel and 17-14CuMo steel after elevated-temperature corrosion test

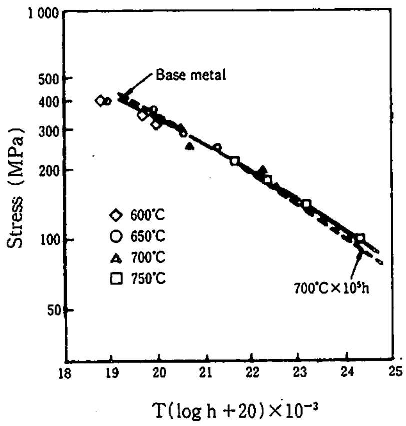


Fig. 11 Creep rupture properties of TIG welded joints of NF709

centration in the chromium oxides observed in the inner layer between the original metal surface and matrix, a thin sulfide layer, a low sulfur concentration, and an extremely thin outer layer mainly composed of iron oxides.

(3) Weldability

The total crack length of NF709 at applied strains of 1% and 2% in the Varestraint test is comparable to that of TP310S. This means that NF709 has the same weld cracking susceptibility as conventional stainless steels composed of single austenite phase.

The creep rupture properties of TIG welded joints of NF709 are arranged by the Larson-Miller parameter and shown in **Fig. 11**. The creep rupture strength at 700°C in 10^4 h is 90 MPa or higher. This means that the creep rupture strength of the weld metal is equal to or higher than that of the base metal.

3.2 Application of tubes in actual boilers

At 352 atm and 649°C, the ultimate target steam conditions of ultra-supercritical boilers, the superheater temperature reaches 700°C. With its huge reserves, coal is relied upon with growing weight as fuel, and the development of coal-fired ultra-supercritical boilers is assuming increasing importance the world over. A solution to this problem is the development of steel tubes with excellent creep rupture strength and corrosion resistance at the elevated temperature of 700°C. In this context NF709 is highly rat in Japan as well as in the United States and Europe, and its service performance is being evaluated in actual boilers. NF709 was authorized by the Ministry of International Trade and Industry, and has been under test in No. 2 boiler at the Oita Thermal Power Plant of Oita Cooperative Thermal Power Co., Ltd. since May 1992.

4. Conclusions

(1) The 9Cr-0.5Mo-1.8W-Nb-V ferritic steel designated NF616 was newly developed. It has 600°C × 10^5 h creep rupture strength that is equal to or higher than that of austenitic stainless steels, and features good as-aged toughness and weldability. It has performed well as tubes in an actual boiler for five years. Great expectations are entertained in this new steel for application to ultra-supercritical boiler tube. It has been under test in an international joint research project.

(2) The 20Cr-25Ni-1.5Mo-Nb-Ti-N austenitic steel designated NF709 was newly developed. It has 700°C × 10^5 h creep rupture strength that is higher than that of the conventional 17-14CuMo steel, exhibits high elevated-temperature corrosion resistance in the coal ash environment, and features excellent as-aged toughness and weldability. It is being evaluated in an international scale for application to ultra-supercritical boiler tubes.

5. Acknowledgments

The authors gratefully acknowledge the cooperation of Tobata Thermal Power Plant of Tobata Cooperative Thermal Power Co., Ltd., Oita Thermal Power Plant of Oita Cooperative Thermal Power Co., Ltd., Mitsubishi Heavy Industries, Ltd., and ELSAM of Denmark in the boiler tests of NF616 and NF709.

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