Mechanical and Corrosion Properties of High Strength 18% Cr Austenitic Stainless Steel Weldment for Boiler

Kazuhiro OGAWA, Yoshiatsu SAWARAGI, Nobuo OTSUKA, Hiroyuki HIRATA, Atsushi NATORI and Shigeru MATSUMOTO¹⁾

Sumitomo Metal Industries, Ltd., Fuso-cho, Amagasaki, Hyogo-ken, 660 Japan.

1) Sumikin Welding Industries, Ltd., Fuso-cho, Amagasaki, Hyogo-ken, 660 Japan.

(Received on April 17, 1995; accepted in final form on June 19, 1995)

The properties of weld metal of 18Cr heat resistant austenitic steel containing high copper, niobium and nitrogen were investigated to obtain the matching filler metal for an austenitic stainless steel of 18Cr–9Ni–3Cu–Nb–N steel. This 18Cr–9Ni–3Cu–Nb–N steel tube has been registered as KA-SUS304HJ1TB in the Japanese official standard for fired power plant materials. This steel tube has a high temperature strength 1.4 times as high as the conventional 18Cr steel ASME TP347H. Welding material applicable to this steel is necessary in the fabrication. However, the weld metal consisting of the same chemistries as the base metal had a lower strength than that of the base metal. In this work, the effect of chemistries of molybdenum and nitrogen on the strength of weld metal was investigated. The addition of molybdenum up to 1 mass% was effective for improving the strength without a deterioration of the corrosion resistance. The nitrogen was also effective for improving the strength, but the nitrogen can be decreased by vaporizing during tungsten inert gas arc welding. For improving the solubility of nitrogen in the molten pool, the addition of manganese was effective. From these findings, the chemistry of welding material was determined as 18Cr–16Ni–3Cu–1Mo–3Mn–0.6Nb–0.2N and the tube weldment with that welding material was evaluated in terms of mechanical properties including creep rupture property. It was confirmed that the weldment had comparable properties to the base metal.

KEY WORDS: austenitic stainless steel; weldment; weld metal; creep; tensile strength; corrosion resistance; boiler tube.

1. Introduction

Because of the intense interest in problems of the earth environment such as the increase of carbonic acid gas, improvement of heat energy efficiency is required in fossil-fired power plants. USC (Ultra super critical) boilers operated under the condition of a temperature over 600°C and steam pressure over 24 MPa are expected as one of the higher heat efficiency plants. For the tube materials applied in the boilers operating at higher temperatures and in higher steam pressures, the improvement in strength at elevated temperature is preferable due to avoiding the increase of wall thickness when using conventional austenitic stainless steel such as Type 347H or Type 321H for super heater or reheater tubes.

A new austenitic stainless steel of 18%Cr–9%Ni–3%Cu–0.5%Nb–0.1%N¹⁾ has been developed for high strength tube material at elevated temperatures and has been registered as KA-SUS304J1HTB in the Japanese official standard for fired power plants.²⁾ In the base metal, the effects of copper, niobium and nitrogen on the high temperature properties have been investigated from a metallurgical point of view.¹⁾ In this report, the effects of chemistries on the weld metal properties was

investigated to obtain the weld metal having comparable properties to the base metal of this new steel.

2. Experimental

2.1. Materials

18%Cr–9%Ni–3%Cu–0.5%Nb–0.1%N austenitic stainless steel tubes were employed, of which sizes were 45 mm in diameter and 6 mm in thickness and 54 mm in diameter and 12 mm in thickness. The chemistry and mechanical properties are shown in **Tables 1** and **2**. The

Table 1. Chemistry of tube tested. (mass%)

	C	Si	Mn	P	S	Ni	Cr	Cu	Mo	Nb	N
Tube	0.10	0.11	0.73	0.018	0.001	9.1	18.4	3.03	—	0.45	0.08

Table 2. Mechanical properties of tube tested. (mass%)

Pipe size	Yield strength (MPa)	Tensile strength (MPa)	Elongation (%)
45 mm in diameter 6 mm in thickness	250	628	65

Table 3. Chemistries of welding materials and plates tested. (mass%)

	C	Si	Mn	P	S	Cu	Ni	Cr	Mo	Nb	N
Alloy A	0.10	0.10	1.01	0.005	0.002	2.96	16.61	18.46	1.02	0.68	0.11
Alloy B	0.10	0.11	1.01	0.005	0.004	2.96	18.00	18.45	12.49	0.70	0.10
Alloy C	0.09	0.10	0.97	0.003	0.002	2.93	16.98	18.25	2.43	0.28	0.09
Alloy D	0.11	0.12	1.00	0.003	0.005	2.95	17.15	17.81	1.09	0.59	0.18
Alloy E	0.10	0.12	3.13	0.003	0.005	2.98	16.45	18.07	1.09	0.65	0.22
Alloy F	0.14	0.12	1.00	0.003	0.005	2.92	17.29	18.20	1.02	0.69	0.20

Fig. 1. Allowable tensile stress of 18Cr-9Ni-3Cu-Nb-N steel tube and its strengthening mechanism.

material was melted in an electric furnace and refined by the vacuum oxygen decarbonization (VOD) process. The tubes were manufactured using hot extrusion and cold draw process in an actual mill and were solution treated at 1150°C. The creep rupture strength of this steel is strengthened by the fine precipitation of ϵ -Cu phase, and that of NbCrN by the alloying of copper of 3 mass%, niobium of 0.5 mass% and nitrogen of 0.1 mass% as well as by the solution strengthening of nitrogen, as shown in **Fig. 1**.¹⁾ The precipitation of NbCrN also improves the deterioration of creep ductility through reducing the grain size. The allowable tensile stress of this steel in the temperature range of 600 to 700°C where allowable stress is determined by the creep rupture strength is 40% higher than that of conventional austenitic stainless steel SUS347H as shown in **Fig. 1**. Moreover below 600°C where the allowable tensile stress is determined by the tensile property, this steel has a high strength due to the solution strengthening by nitrogen.

Welding materials tested were melted in the vacuum furnace and rolled to a wire of 1.2 mm in diameter. Some of these were hot forged and rolled to the 10 mm thick plates for the bead-on-plate welding test. The chemistries are shown in **Table 3**.

2.2. Testing

2.2.1. Tube Welding Test

The girth welding of the tubes was conducted using the tungsten inert gas (TIG) arc welding process with the various welding materials to be tested. The weld heat input was about 0.97 kJ/mm. To evaluate the effect of

Table 4. Hot corrosion test condition simulating coal fired boiler.

Ash	Na ₂ SO ₄	37.5	(mass%)
	K ₂ SO ₄	37.5	(mass%)
	Fe ₂ O ₃	25	(mass%)
	Coating thickness	30	(mg/cm ²)
Gas	SO ₂	0.25	(ppm)
	O ₂	3	(%)
	CO ₂	15	(%)
	N ₂	bal.	(%)
Temperature	650	(°C)	
Duration	7 200	(s)	

interpass temperature on the strength of the weldment, welding was first conducted under the condition of interpass temperature of 150°C by cooling each pass, and secondary without cooling any interpass resulting in a temperature of 650°C, which was measured after final pass. Pure argon gas was employed as the torch shielding gas in TIG welding except for some joints, which were welded using argon gas containing 1, 2 or 10% nitrogen gas for torch shielding gas to investigate the effect of nitrogen content in weld metal on the tensile strength.

The welded joints obtained were evaluated in terms of tensile properties at room temperature and elevated temperatures of 550°C, Vickers hardness distribution, and creep rupture strength. The following test specimens were machine produced from the tube welded joints. The tensile test specimen and creep rupture test specimen had a parallel part 6 mm in diameter and 30 mm in length with the weld metal in the center of the parallel part.

2.2.2. Corrosion Test

The corrosion test was conducted using the 3 mm thick and 15 mm square test specimen machined from the overlay weld metal, which was produced by 4 layered welding using the TIG welding process with the welding materials to be tested and with a weld heat input of 1.1 kJ/mm. The corrosion test condition simulating a coal fired boiler environment⁶⁾ is shown in **Table 4**. The corrosion resistance was evaluated by measuring the weight loss of the specimens.

2.2.3. Evaluation of Nitrogen Reduction by Welding

The reduction of nitrogen content by welding was evaluated. The nitrogen content was analyzed in the weld metal produced by TIG bead-on-plate welding without filler metal using the 10 mm thick plate shown in **Table 3**. The shielding gas employed was pure argon and the

weld heat input was about 1.4 kJ/mm.

3. Effects of Chemistries of Weld Metal on Properties

To determine the proper chemistries of welding material, the effects of molybdenum and nitrogen on the strength and corrosion resistance of the weld metal were investigated.

3.1. Hardness of Weld Metal

Hardness distributions in welded joints were evaluated to investigate the proper chemistry to obtain as high a tensile strength in the weld metal as the specified value in the base metal. The results under the various interpass temperature conditions using the 12 and 6 mm thick tubes are shown in Fig. 2. All the weldings were conducted employing the TIG process and the 18%Cr–16%Ni–3%Cu–1%Mo–0.6%Nb–0.1%N welding material of Alloy A in Table 3 with the weld heat input of 0.97 kJ/mm. The hardness of the weld metal and heat affected zone (HAZ) in the 12 mm thick tube welded joints were as high as 220 in Vickers hardness number. The 6 mm thick tube welded joints had a lower hardness of weld metal than the 12 mm thick one even at the same interpass temperature condition of 150°C. The joint on the interpass temperature condition of 650°C had a lower hardness of weld metal than that of 150°C. The reason for the hardness of the weld metal varying with the tube thickness and the interpass temperature is understood by considering the effect of work hardening in austenitic steel. Essentially the weld metal consisting of as solidified

and coarse grain austenitic microstructure has a lower strength than the base metal with a sufficiently refined microstructure. However, in the large thickness tube the weldment can be work hardened by the weld thermal strain caused by the restraint of thermal deformation, therefore the hardness can be increased by multipass welding. But in the smaller thickness tube and on the higher interpass temperature condition, the less effective the work hardening by the restraint can be and therefore the weld metal has a lower hardness. Figure 3 shows the microstructure of weld metals observed with transmission electron microscope (TEM) using thin foil. The weld metal on the interpass temperature condition of 150°C had a higher dislocation density than the weld metal on that of 650°C. This result suggested that on the lower interpass temperature condition a more effective work hardening is produced and supported the hardening mechanism mentioned above. Considering practical use, the tensile strength of weld metal can be insufficient in a thin wall tube on the high interpass temperature condition. The improvement of weld metal strength was investigated from the point of view of the chemistry of welding material.

3.2. Corrosion Resistance of Weld Metal

The effect of molybdenum to be added to improve the strength of weld metal on the corrosion resistance in the environment simulating the coal fired boiler was evaluated as shown in Fig. 4. In this figure the tensile strength of the welded joint was also plotted and these

a) 12mm thick tube welded with interpass temperature of 150°C

b) 6mm thick tube welded with interpass temperature of 150°C

c) 6mm thick tube welded with interpass temperature of 650°C

Fig. 2. Hardness distribution of welded joints using welding materials of Alloy A.

a) Interpass temperature of 150°C

b) Interpass temperature of 650°C

0.25 μm

Fig. 3. Microstructure of weld metal on various interpass temperature conditions observed with TEM using thin foil.

Fig. 4. Effect of molybdenum on tensile strength and corrosion resistance of weld metal on interpass temperature condition of 650°C.

strength indicated the strength of the weld metal because the fractured portion was at the weld metal. The corrosion loss of the weld metal including molybdenum over 1 mass% was higher than that of the base metal, though the molybdenum addition increased the tensile strength of the 6 mm thick tube welded joint which was produced on an interpass temperature condition of 650°C. The deterioration in corrosion resistance by the excess addition of molybdenum is assumed to be due to the increase in oxidation potential of the alloy matrix. From these results, the allowable quantity of molybdenum to improve the strength of the weld metal was determined as 1 mass%.

3.3. Strengthening by Nitrogen Addition

The improvement of weld metal strength by the addition of nitrogen from shielding gas was investigated, which is regarded as effective in austenitic stainless steel. Figure 5 shows the tensile strength of 6 mm thick tube welded joint on the interpass temperature condition of 650°C plotted against the nitrogen content in the weld metal. By the nitrogen addition the tensile strength of the welded joint was improved, though most of the joints fractured at weld metal in the tensile test. In this case, the tensile strength of weld metal, including the nitrogen content over 0.12 mass%, satisfied the target values of 588 MPa at room temperature and of 446 MPa which are minimum strength specified in the base metal. In the actual fabrication pure argon is employed as a shielding gas of TIG welding, so the nitrogen addition is to be alloyed in the welding materials, not provided by the shielding gas. However, alloyed nitrogen can be decreased by the TIG welding process so the nitrogen content in the weld metal is not always as much as in the welding material.³⁾ Figure 6 shows the comparison of the nitrogen content in the base metal plate and in the weld metal remelted by TIG arc without filler metal. The nitrogen content was reduced to about 80% by the TIG welding, and the manganese addition helped to increase the residual quantity of nitrogen. In the TIG arc atmosphere protected from the air by argon shielding gas, nitrogen in a molten pool can be just degasified

Fig. 5. Effect of nitrogen content in weld metal including 1% molybdenum on tensile strength of welded joint.

Fig. 6. Comparison of nitrogen content in bead-on-plate weld metal and in base metal plate of 18Cr-16Ni-3Cu-2Mo-Nb-N steel.

without absorption, as the partial pressure of nitrogen is extremely low. It is reported that manganese has the effect of increasing the solubility of nitrogen in molten steel.^{4,5)} It is assumed that the decrease of nitrogen occurs due to the vaporization from the molten pool by welding and that the vaporization was partially prevented due to the increase of nitrogen solubility by the addition of manganese. As a result, considering the reduction by welding and dilution by the base metal including the nitrogen content of 0.1 mass% the nitrogen content of the welding material should be over 0.2 mass%.

3.4. Proper Chemistry of Welding Material

From these findings the chemistry of welding material was determined as 18%Cr-16%Ni-3%Cu-1%Mo-3%Mn-0.6%Nb-0.2%N, which corresponds to Alloy E in Table 3. The chromium and copper content were determined referring to the base metal. The nickel content was increased up to 16 mass% on the basis of the phase stability. The weld metal includes 3 mass% manganese and 1 mass% molybdenum which can help to produce intermetallic compound such as sigma phase during heating in elevated temperature in service. Therefore sufficient nickel was alloyed to obtain the phase stability.

4. Properties of Welded Joint

The girth welded joints of 6 mm thick tube were produced employing the TIG process with the welding material of Alloy E shown in Table 3 and pure argon shielding gas on the interpass temperature condition of 650°C. The joints were evaluated in terms of their mechanical properties including the creep rupture strength.

4.1. Hardness Distribution

The hardness distribution of the welded joint is shown in Fig. 7. The weld metal had about 180 in Vickers hardness number comparable to the base metal.

4.2. Tensile Strength

The tensile strength of the welded joint is shown in Fig. 8. The welded joint had high enough strength to satisfy the minimum value specified in the base metal at elevated temperature such as 550°C as well as at room temperature. The fractured portions in the tensile test were weld metal at room temperature and base metal at the elevated temperature respectively.

4.3. Creep Rupture Properties

The creep rupture properties of the welded joint at 600 to 700°C are shown in Fig. 9. The rupture strength of the welded joint was within the scattered range of base metal data. All the welded joints ruptured at the base metal, as shown in Fig. 10. The microstructure of the ruptured portion and the weld metal of the creep rupture

tested specimen were observed. Figure 11 shows the example ruptured at 650°C for 24.7 Ms (3 244 h). A large number of creep voids at the grain boundary were observed in the vicinity of the ruptured portion of the base metal. However, creep voids were scarcely observed in the weld metal. The precipitates in the base metal and weld metal creep tested were observed with TEM using extraction replica as shown in Fig. 12. The fine stringer shape precipitates, identified as NbCrN, were observed in the weld metal as well as in the base metal. The micro-structures of the ruptured specimen were also observed with TEM using thin foil as shown in Fig. 13. A large number of fine particles, which are about 20 nm in diameter and are assumed as ϵ -Cu phase, were observed in high density in the weld metal as well as the base metal. The both kinds of fine particles are considered as effective for the creep strength by precipitation strengthening mechanism. From these results, the weld metal was strengthened by the same mechanism as the base metal during heating in the creep test. Moreover, the weld metal had molybdenum, which is not included in the base metal, and had a higher nitrogen content than the base metal, so that the creep rupture strength of the weld metal exceeded that of the base metal due to the solution strengthening by the molybdenum and additional nitrogen. Therefore, creep rupture occurred not at the weld metal but at the base metal in the welded joint.

5. Conclusion

The weld metal properties of 18% chromium, copper, niobium and nitrogen bearing austenitic stainless

Fig. 7. Hardness distribution of welded joint using welding material of Alloy E.

Fig. 8. Tensile strength of welded joints using welding material of Alloy E.

Fig. 9. Creep rupture strength of welded joint using welding material of Alloy E.

Fig. 10. Cross section of creep rupture specimen of welded joint using welding material of Alloy E ruptured at 650°C for 3 244 h.

a) Ruptured portion in base metal

b) Weld metal

Fig. 11.
Microstructures of welded joint using welding material of Alloy E ruptured at 650°C for 3 244 h.

a) Weld metal

b) Base metal

Fig. 12.
TEM micrographs by extraction replica of welded joint using welding material Alloy E ruptured at 650°C for 3 244 h.

a) Weld metal

b) Base metal

Fig. 13.
TEM micrographs by thin foil of welded joint using welding material of Alloy E ruptured at 650°C for 3 244 h.

steel were investigated and the following results were obtained.

(1) The hardness of weld metal decreased in the welded joint of a lower thickness tube and on the condition of higher interpass temperature.

(2) The molybdenum was effective in improving the tensile strength of weld metal but an addition over 1 mass% deteriorated the corrosion resistance of weld metal in the simulated coal fired boiler environment. Nitrogen addition was effective in improving the tensile strength of weld metal.

(3) The nitrogen content in weld metal decreased to about 80% of that in welding material by vaporization during the TIG welding process. Manganese addition was effective in preventing nitrogen decrease through welding.

(4) From the above findings the welding material

was designed as 18%Cr–16%Ni–3%Cu–3%Mn–1%Mo–0.5%Nb–0.2%N and it was confirmed that this weld metal had as high a tensile and creep rupture strength as KA-SUS304J1HTB tube.

REFERENCES

- 1) Y. Sawaragi, K. Ogawa, S. Kato *et al.*: *Sumitomo Search*, (1992), No. 48, 50.
- 2) Notification for Providing the Details of Technical Standards for Thermal Power Generating Facilities, Japanese Ministry of Trade and Industry, (1994).
- 3) J. A. Brooks: *Weld. J.*, **54** (1975), No. 6, 189s.
- 4) S. Kobayashi, T. Kuwana *et al.*: *J. Jpn. Weld. Soc.*, **50** (1971), 308.
- 5) F. Ishii, S. Banya and T. Fuwa: *Tetsu-to-Hagane*, **68** (1982), 1551.
- 6) H. Fujiwaka and H. Makiura: *J. Mater. Energy Syst.*, **4** (1982), No. 3, 160.