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A NEW AUSTENITIC TUBE ALLOY CONTAINING 9% MOLYBDENUM RESISTANT TO FIRESIDE CORROSION IN WASTE INCINERATORS

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A 22%Cr-52%Ni-9%Mo-0.8%Nb alloy was developed for superheater tube application in Waste-to-Energy plants. This tube alloy was designed to improve thermal stability of Alloy 625 at 600-650℃ while maintaining the excellent high-temperature corrosion resistance of alloy 625 in waste incinerators. Laboratory corrosion tests revealed that iron content of 3-20 mass% Fe did not alter the corrosion resistance of high-Ni high-Mo alloys. The developed alloy had an equivalent corrosion resistance to alloy 625 in waste incinerator corrosion environment. The Gleeble test, tensile test, creep rupture test up to 10^4 h, and Charpy impact test for aged materials upon aging were performed for this alloy; test results showed that this alloy can be used as boiler tubes up to 650℃. Test results of the tube alloy produced by conventional tube manufacturing processes were demonstrated as well.

1. INTRODUCTION

In Japan, attention has been paid on the energy recovery upon incineration of municipal and industrial solid waste since people become aware of the potential energy of solid waste[1,2]. To increase the efficiency of energy conversion upon incinerating solid waste, several attempts have been made to raise the steam temperature and pressure of heat recovery boilers, but higher steam temperature resulted in severe fireside corrosion especially of superheater tubes. In Japanese conventional heat-recovery boilers, superheater tubes of carbon steel have been widely used, and the steam temperature at the outlet superheater section is limited to around 300℃ to prevent high temperature corrosion of tube materials.

Recently, in a newly-introduced waste-to-energy (WTE) plant at Koshigaya, Saitama-east, a challenge has been made to adopt the steam temperature of 380℃ with using a modified 310 stainless steel tube (Sumitomo HR3C) at high temperature superheater section[3]. In terms of fireside corrosion of superheater tubes, this material, along with boiler design and operation, has demonstrated an excellent performance with the maximum corrosion thickness loss of only 0.51 mm in three years[3]. In another WTE plant built in Obihiro, Hokkaido, which generates 400℃ steam, SUS310S stainless steel was used as tertiary superheater tubes where the steam temperature is the highest[4]. The maximum thickness loss of SUS310S superheater tubes is reported to about 0.45mm in two years[4], suggesting that stainless steels of 310 family can perform good in WTE plants of 400℃ steam. In a project directed by Tokyo metropolitan government, corrosion tests were conducted in a waste heat boiler firing municipal solid waste. Superheater bundles were placed in a boiler, the outlet steam temperature of which was set to 450℃. Test results showed that the maximum corrosion rate of stainless steels of 310 family was 0.6 mm/year if the superheater bundles are located in a proper position where the flue gas temperature is below 620℃[5]. In a Japanese national project funded by NEDO, attempts have been made to establish technology for advanced WTE plant which has the net efficiency of 30%. For this purpose, steam condition of 500℃, 100 ata is targeted, and various corrosion-resistant superheater materials were evaluated[6]. In this project, conventional and newly-developed high-Ni alloys have been tested in a demonstration plant built at Tsukui, Kanagawa; the steam temperature of its boiler was 500℃. Superheater bundles were manufactured by various corrosion-resistant alloys and tested in the boiler for about two years, The corrosion environment of this 500℃ steam boiler has turned out to be extremely harsh; the maximum corrosion rates of conventional/newly developed high-Mo high-Ni alloys (such as alloy 625) were 0.7- 0.9 mm in 6400h operation[7]. The test results clearly suggest that to combat fireside corrosion in advanced WTE boilers, high-Mo high-Ni alloys are needed, along with good boiler design and careful operation. Hence, for boilers of up to 450℃ steam, stainless steels of 310 family may be applicable, but for boilers of 500℃ steam, high-Mo high-Ni corrosion resistant alloys (CRA) are required for superheater materials in advanced WTE plants.

As summarized by Sorrel[8], fireside corrosion of boiler tubes in WTE plants is considered to result from corrosive fuel-slag deposits of sulfate and chloride mixtures, which contain alkali metals (Na, K) and heavy metals such as Pb and Zn. Oxidizing gas species such as HCl, SO_2, O_2, and H_2O in flue gases are considered to contribute to the corrosion reaction as well. The corrosion can be interpreted as "hot corrosion" caused predominantly by low melting-point temperature species (fused salts) in the slag deposits, but gaseous corrosion caused predominantly by Cl_2 generated upon reaction of HCl and O_2 in flue gas (the Deacon reaction)[9] can dominate in some cases.

Corrosion resistance of steels and alloys in this environment is reported by the current author[10]. Otsuka et al. have conducted series of laboratory corrosion tests at 400-550℃ by using synthetic ashes. They demonstrated that addition of Mo to high-Ni alloys reduced the corrosion rate at 550℃.

Generally, among high-Mo alloys, alloy 625 was favored for application to superheater tubes in WTE boilers since this alloy was approved in ASTM specification (B444) and is included in ASME Boiler and Pressure Vessel Code.

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Although the corrosion resistance of alloy 625 for use as superheaters in WTE boilers is considered good, malleability of this alloy is indeed relatively poor, and manufacturing seamless tubing is somewhat difficult and troublesome. In addition, alloy 625 loses its ductility after long-term exposure to high temperatures, leaving questions on thermal stability as high temperature materials. Since alloy 625 has "extraordinary" high strength at both low and high temperatures, fabrication such as hot/cold bending is usually not easy. Hence, high-Mo alloy with equivalent/better corrosion resistance, good thermal stability, and moderate high/low temperature strength is needed for the purpose.

2. MATRIALS AND METHODS

Tubes with an outer diameter of 48.8 mm, a wall thickness of 9.5 mm, and a length of 5000 mm were manufactured for alloy A and B designated in Table 1 by hot extrusion process at Sumitomo Metal Steel Tube Works. After hot extrusion, cold rolling followed, with a solution heat treatment at 1130℃. The chemical composition, along with the specification of the tube alloy, is presented in Table 1. The niobium content was kept between 0.51-1.0% to ensure good hot ductility upon forging, rolling, and extrusion processes necessary for production of seamless tubing. For comparison, commercial alloy 625 tube was tested. Four experimental alloys, the chemical composition shown in Table 1, were prepared by vacuum induction melting from electrolytic Fe, Ni, Cr, etc. Ingots (20kg) were hot forged to make slabs of 20 mm thick. After softening heat treatment at 1100℃ for 1 h, the slabs were cold rolled to a thickness of 15 mm. The solution heat treatment was at 1150℃ followed by water quenching. Mechanical and corrosion test specimens were cut from the middle of the tube and plate wall. Specimens for the tensile tests and creep rupture tests were round bars of 6 mm outer diameter with a gauge length of 30 mm, while the dimensions of the V-notched Charpy impact test specimens were 5 x 10 x 50 mm. Greeble test specimens (round bars of 6mm outer diameter) were cut from the slabs before softening heat treatment. To investigate the embrittlement behavior of these alloys upon aging, aging heat treatments were conducted at 550, 600, 650, and 700℃ for up to 10000 h. Creep rupture tests were performed at 550, 600, 650, 700, and 750℃ under constant loads. Specimens for high temperature corrosion tests were 15 x 15 x 3 mm. Synthetic ashes of 6.0%Cl and 9.1%Cl, the composition of which is shown in Table 2, were coated on the entire surface of the specimen using acetone. The amount of the deposit was 30 mg/cm^2 per unit specimen surface area. The corrosion tests were conducted by heating specimens in a simulated flue gas atmosphere of 1500ppm HCl-300ppm SO_2-7.5%O_2-7.5%CO_2-20%H_2O-bal.N_2 at 550℃ for 20 h. After tests, specimens were chemically descaled, and corrosion weight loss was measured by a microbalance. Detailed corrosion test procedures were described elsewhere[9]. To evaluate weldability of the alloy, the Trans-Varestraint test was performed, and the maximum crack length was measured to evaluate weldability of the developed alloy.

Table 2. Synthetic ashes used in this study

ash	composition mol %	Cl wt.%	S as SO_3 wt.%
chloride (A)	30%$PbCl_2$-30%$FeCl_2$--20%NaCl-20%KCl	38.3	0
sulfate (B)	37.5%Na_2SO_4-37.5%K_2SO_4-25%Fe_2O_3	0	37.9
6.0%Cl	mixture of ash A and ash B (1:5)	6.0	31.9
9.1%Cl	mixture of ash A and ash B (1:3)	9.1	28.9

3. RESULTS AND DISCUSSIONS

3.1 Alloy design

The chromium, molybdenum, and aluminium contents of the laboratory-melted alloys were fixed at 21, 8.5, and 0.2 % respectively to follow the alloy composition of alloy 625. To improve hot workability of alloy 625, niobium content was lowered to below 1.0%. Alloy 625 is reported to lose thermal stability upon aging at high temperatures through precipitation of sluggish nickel-niobium-rich gamma prime phases[12], which transform to orthorhombic Ni_3Nb heated for long times. To improve thermal stability of alloy 625, alloys with low niobium were prepared. Alloys with low nickel content were prepared from economic reason as well.

3.2 Hot ductility

The Greeble test, a high temperature tensile test with high strain rates, was performed to clarify the hot-working characteristics of the alloys. Alloy 625 lost its ductility at above 1150℃ and became susceptible to cracking. However, the developed alloy maintained its ductility for up to 1250℃ and the ductility values, indicated by reduction in area, were more than 60% at 1150-1250℃, indicating that the developed alloy has satisfactory ductility for forging, hot rolling, and extrusion processes required for production of seamless tubes and plates. This is interpreted to result from the relatively low niobium content of the alloy, which enabled minimal precipitation of metastable body centered cubic gamma double prime phases(γ'')[13].

3.3 Tensile test results

Tensile test results of the developed tube alloy for up to 800℃ are shown in Fig. 1. Tensile strength of the developed alloy at RT was 650-750 MPa, which is much less than alloy 625 (for annealed material, i.e., 823-965 MPa[12]). This suggests that fabrication of this tube alloy to boiler tube bundles by cold bending is much easier to perform than alloy 625 tubing. Tensile strength of the developed alloy at 550℃ was 480-580 MPa, slightly higher than the conventional austenitic boiler tube steel of SUS347HTB. The strength of this alloy is considered to result from solid-solution strengthening of dissolved molybdenum, which have contributed to an increase in the tensile strength of the alloy.

Table 1. Chemical composition of the developed alloy (mass %)

	C	Si	Mn	P	S	Ni	Cr	Mo	Nb	Fe	Al
specification	≦0.03	≦0.50	≦0.50	≦0.015	≦0.003	bal.	20.0/23.0	8.0/10.0	0.51/1.0	15.0/20.0	≦0.4
alloy A	0.017	0.21	0.20	0.008	<0.001	52.18	21.81	8.55	0.69	16.42	0.25
alloy B	0.016	0.20	0.20	0.009	<0.001	51.78	21.85	8.82	0.87	16.32	0.25
alloy 625	0.04	0.40	0.38	0.002	0.002	60.25	21.61	8.99	3.68*	-	0.19
XZ17**	0.02	0.31	0.49	0.006	0.003	58.06	21.29	8.70	0.20	10.77	0.16
XZ25**	0.01	0.22	0.20	0.005	0.001	56.40	21.06	8.44	0.59	11.02	0.18
XZ26 **	0.01	0.23	0.20	0.006	0.001	47.76	21.11	8.45	0.58	19.68	0.18
WW3**	0.02	0.31	0.29	0.011	0.002	59.81	21.33	9.00	-	8.82	0.19

* Nb+Ta, **experimental alloy

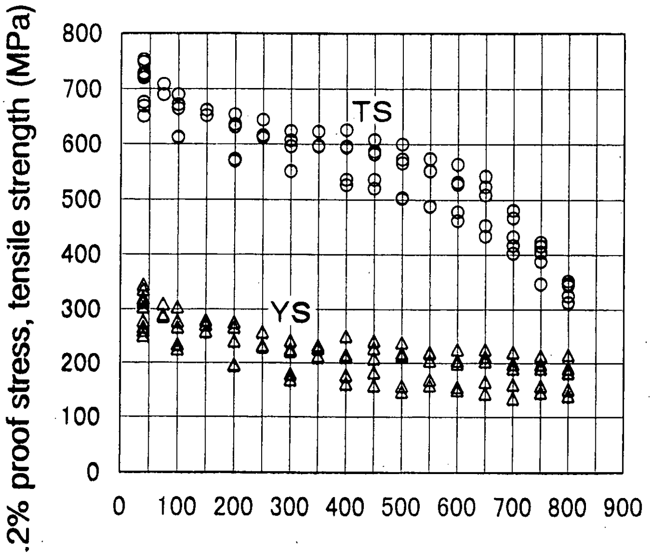

Figure 1. Tensile test results of the developed alloy

3.4 Creep rupture strength

The creep rupture test results of the tube alloy are summarized in Fig.2 These data were plotted according to the Larson-Miller parameter and are shown in Fig. 3. The extrapolated 10^5 h creep rupture strength at 600 and 650℃ was 156, and 106 MPa, whereas those of the annealed alloy 625 are reported 365(at 593℃) and 179 MPa (at 621℃)[12]. For SUS347HTB steel for comparison, they are 152(600 ℃) and 77MPa(650℃) respectively. The creep rupture strength of the developed alloy is less than the annealed alloy 625, but is comparable or even better than the conventional SUS347HTB steel.

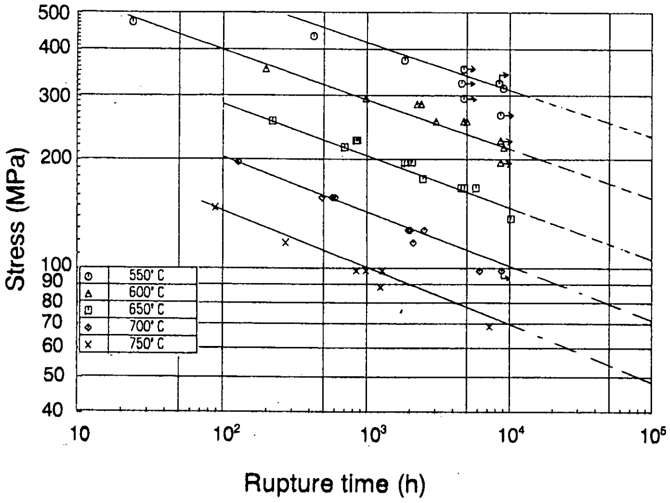

Figure 2. Creep rupture test results of the developed alloy

3.5 Embrittlement upon aging

Results of Charpy impact tests conducted at 0℃ for the aged specimens at 550, 600, 650, and 700℃ for 10000 h are shown in Fig. 4. For the developed alloy, the aged materials maintained good toughness of more than 40 J/cm^2 heated for up to 650℃ for 10000 h while alloy 625 lost its toughness when heated above 600℃ for 10000 h. The test results clearly show that the developed alloy might be applicable to superheaters of steam generating boilers for metal temperatures of up to 650℃. In contrast, the conventional alloy 625 loses its toughness upon aging at above 600℃.

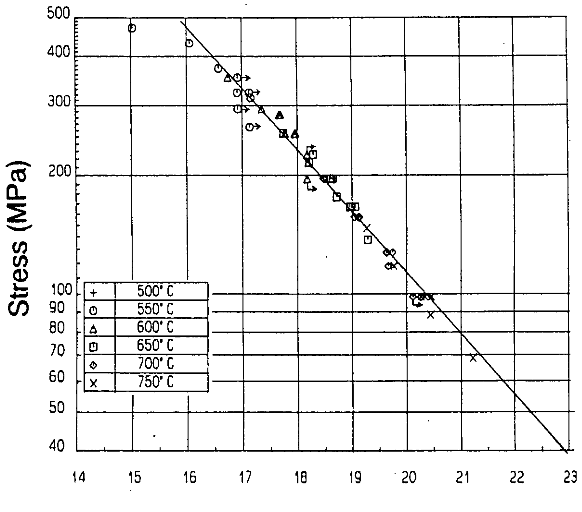

Figure 3. Larson-Miller parameter curves for the developed alloy

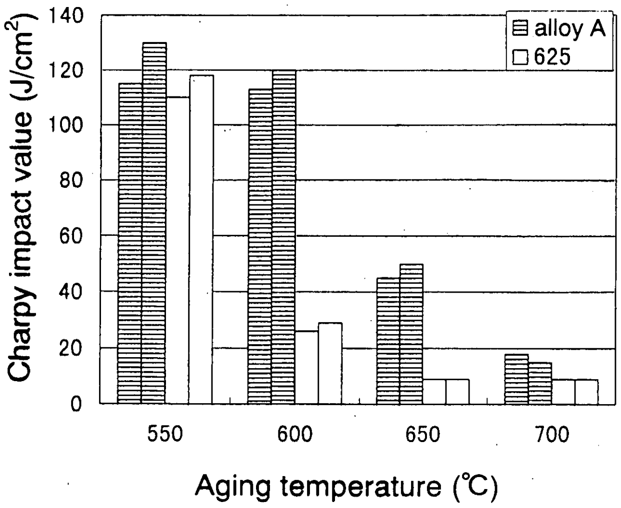

Figure 4. Charpy impact test results at 0℃ of the aged developed alloy (heated for 10000 h)

3.6 High temperature corrosion resistance

Laboratory corrosion test results of the developed alloy are shown in Figs. 5 and 6. Figure 5 presents the effect of Fe content on the corrosion resistance of the alloys. Clearly, the effect of Fe content between 4-20 mass % did not alter the corrosion resistance of the alloy significantly. The effect of niobium on the corrosion resistance of high-Mo alloy is presented in Fig.6. Similar to Fe, niobium content between 0-4 mass% did not virtually change the corrosion resistance of high-Mo alloys drastically. These test results confirm that the corrosion resistance of the developed alloys A and B are comparable to alloy 625 in simulated waste incinerator corrosion environments.

These test results could be interpreted as follows; the corrosion resistance of high-Mo alloys is affected predominantly by Mo[10]. The effects of Ni (45-65%) and Nb(0-4%) on corrosion are minor. Microscopic observation revealed that grain boundary attack usually found

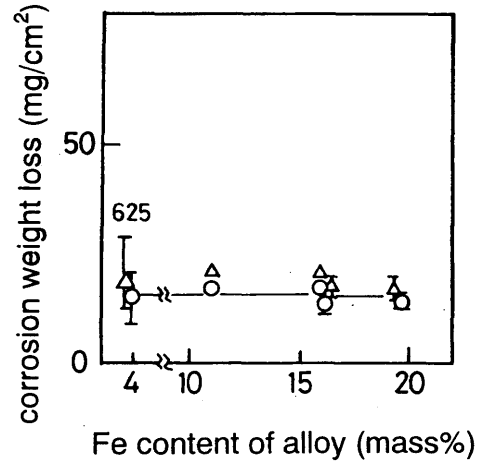

Figure 5. The effect of Fe content on the corrosion resistance of 21Cr-bal.Ni-9Mo-0.7Nb-xFe alloys reacted with sulfate/chloride salt at 550℃ doe 20 h (○:9.1%Cl ash, △:6.0%Cl ash).

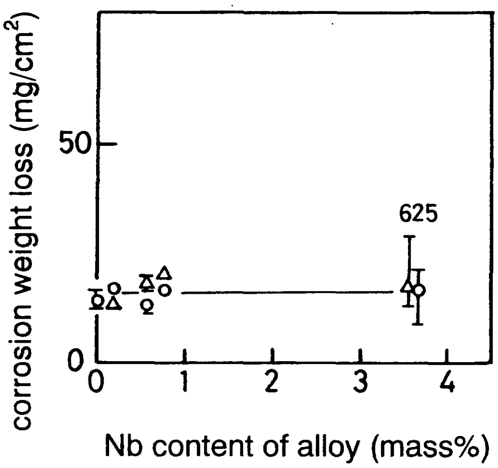

Figure 6. The effect of Nb content on the corrosion resistance of 21Cr-bal.Ni-9Mo-xNb-8/20Fe alloys reacted with sulfate/chloride salt at 550℃ doe 20 h (○:9.1%Cl ash, △:6.0%Cl ash).

on austenitic steels and alloys[11] in waste incinerator corrosion environments was minimal for the developed steels while some intergranular attack was observed for alloy without Nb addition (alloy WW3). This could be explained by the fact that addition of Nb is needed to stabilize carbon in the alloy to avoid grain boundary attack caused by chloride fused salts in the fireside tube deposits. Hence, for the developed alloy, niobium of 0.51-0.1 mass % was added intentionally.

3.7 Weldability

The maximum crack length found for the developed alloy upon Trans-Varestraint test of 2% strain was around 0.9 mm, which is equal to SUS310S steel. From the point of weldability, the developed alloy was completely satisfactory.

4. CONCLUSION

A 22%Cr-52%Ni-9%Mo-0.8%Nb alloy was developed for application to superheater tubes in Waste-to-Energy plants. This alloy was designed to improve thermal stability of alloy 625 at 600-650℃ while maintaining the excellent high-temperature corrosion resistance of alloy 625 in waste incinerators. Laboratory corrosion tests revealed that iron content of 3-20 mass% did not alter the corrosion resistance of high-Ni high-Mo alloys; the developed alloy had equivalent corrosion resistance compared with alloy 625. The tensile test, creep rupture test up to 10^4 h, and Charpy impact test for aged materials were performed for this alloy. Test results showed that this alloy can be used as boiler tubes for up to 650℃. The developed alloy can be welded satisfactory using tungsten inert gas (TIG) procedures, and the crack sensitivity upon welding was about the same as that of SUS310S steel. This alloy was successfully manufactured by the conventional hot extrusion process, normally used for production of seamless boiler tubes. Tube manufacturing was completely satisfactory.

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