Development of High Strength Steel Boiler Tube (TEMPALOY AA-1)

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Recent boilers have been designed for higher temperatures and pressures than those in the past and require steels with high temperature strength that is greater than that of conventional 18-8 austenitic stainless steels. The effects of various alloying elements on the creep rupture strength of 18-8 austenitic steels were examined. As a result, a new heat resisting steel (0.1C-18Cr-10Ni-3Cu-Ti-Nb) was developed. The new steel has a creep rupture strength at 600–700 that is 30% higher than that of TP347H. This steel tube, called TEMPALOY AA-1, is expected to be a candidate material for ultra supercritical boilers.

1. Introduction

Recently, the design of thermal power plants has tended towards higher thermal efficiency, prompted largely by concerns over global environmental problems¹⁾. For coal-fired thermal power plants, in particular, USC (Ultra Supercritical) boilers, which use steam at very high temperatures and pressures to achieve higher thermal efficiency, are under construction²⁾. In response to such severe requirements, a high temperature strength steel, KA SUS321J1HTB (TEMPALOY A-1) steel, is used for superheater tubes and reheater tubes for the USC boiler²⁾. This steel offers high temperature strength that is superior to conventional 18-8 austenitic stainless steels. Now, even more severe steam conditions are under study³), and a heat resisting tube will be demanded that has even greater high temperature strength and more stable longterm strength and microstructure to provide even higher economic efficiency.

It has been reported that if copper is added to 18-8 austenitic stainless steel, fine precipitates of Cu-rich phase that appears at service temperatures can be used with a resultant improvement of creep rupture strength⁴⁾. NKK studied the effects of varying alloying elements such as Cu, P and C in KA SUS321JIHTB steel on creep rupture strength and ultimately developed a "new austenitic stainless tube with superior high temperature strength," named TEMPALOY AA-1.

This paper discusses various properties of this new alloy and factors affecting high temperature strength.

2. Objective of development and effects of alloying elements

2.1 Objective of development

When used for superheater tubes with a 45.0 mm outside diameter and 11.25 mm thickness, KA SUS321J1HTB steel can accommodate a steam condition of 593 -30 MPa. However, if the steam temperature is further raised to about 630 , this alloy steel can no longer be used. Accordingly, the development objectives were set as follows.

 (1) The new alloy can be used for superheater steam tubes under steam conditions of 630 -30 MPa, while providing an allowable stress at 675 of at least 54 N/mm².
(2) Various properties of the new alloy, such as workability and welding properties, should be comparable to KA SUS321J1HTB steel.

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(3) The new alloy should have good economic efficiency.

These represented the basis of alloying element composition design.

2.2 Effects of alloying elements on creep rupture strength of the 18Cr-8Ni austenitic stainless steel

Precipitation strengthening, solution strengthening and a small amount element strengthening are possible methods for improving the creep rupture strength of austenitic stainless steel. Carbide precipitation in the form of $M_{23}C_6$, NbC, TiC and nitride precipitation in NbN, NbCrN are representative cases of precipitation strengthening. Modified precipitation strengthening of the Cu-rich and -prime phases is also known⁵). **Fig. 1** shows the effect of adding only Cu to 18-8 austenitic stainless steel on creep rupture strength. The figure shows that the addition of 3 weight percent copper increases the creep rupture strength; but the effect of further increasing the copper content is marginal.

Mo and W are well-known alloying elements for producing solution strengthening. P, B and various alloying elements have also been studied for providing a small amount element strengthening⁵.

Based on this information, the development work studied the effects of alloying elements on creep rupture strength using eight materials for the melting test, as shown in **Table 1**. 18Cr-8Ni austenitic stainless steel was selected as the base metal for economic reasons. The composition was designed as follows. Nb and Ti were added (0.25Nb-0.1Ti) to produce MC carbide precipitation strengthening. At the same time, 3 weight percent copper was added to provide precipitation strengthening of Cu-rich phase. Tests were conducted to clarify the effects of P (CP25–CP85) and C (CC1P2–CC4P2) variations on the creep rupture strength using this alloy as the base composition.

2.2.1 Effect of P on creep rupture strength

Fig. 2 shows the effect of P on the creep rupture strength of the 18Cr-8Ni-3Cu-Ti \cdot Nb steel. The figure indicates that the addition of P increases the creep rupture strength. This may be attributable to particles of precipitated M₂₃C₆ and MC carbides becoming smaller as a result of the P addition⁵).

Fig. 3 shows the effects of P on creep rupture elongation. The high P steels that show high rupture strength are all low in creep rupture elongation, indicating that their high temperature ductility needs improvement before they can be put to practical use. For this reason, the content of P was set at 0.025%.

2.2.2 Effect of C on creep rupture strength

Fig. 4 shows the effect of C on the creep rupture strength of the 18Cr-8Ni-3Cu-Ti \cdot Nb steel. The effect of C is not noticeable at 650 or 700 . Over the range of C content tested, the difference in C content



Fig. 1 Effect of Cu content on creep rupture strength of 18-8 austenitic stainless steels



Fig. 2 Effect of P content on creep rupture strength

												(n	nass %)
Steel	С	Si	Mn	Р	S	Cu	Ni	Cr	Mo	Nb	Ti	В	N
CP25	0.093	0.21	1.61	0.026	0.004	3.21	7.79	17.93	0.01	0.25	0.13	0.0021	0.0047
CP45	0.095	0.21	1.61	0.053	0.004	3.18	7.69	17.81	0.01	0.25	0.13	0.0022	0.0045
CP65	0.096	0.21	1.61	0.063	0.004	3.24	7.71	17.78	0.01	0.25	0.12	0.0023	0.0047
CP85	0.096	0.21	1.60	0.078	0.004	3.19	7.72	17.79	0.01	0.25	0.12	0.0019	0.0044
CC1P2	0.072	0.22	1.64	0.025	0.004	3.18	7.70	17.72	0.01	0.25	0.12	0.0019	0.0052
CC2P2	0.095	0.22	1.65	0.026	0.004	3.17	7.68	17.76	0.01	0.25	0.12	0.0020	0.0056
CC3P2	0.117	0.23	1.64	0.025	0.004	3.18	7.67	17.70	0.01	0.25	0.12	0.0020	0.0057
CC4P2	0.143	0.23	1.64	0.026	0.004	3.18	7.70	17.74	0.01	0.25	0.12	0.0020	0.0058

Table 1 Chemical compositions of steels studied



Fig. 3 Effect of P content on creep rupture elongation

does not appreciably affect the $M_{23}C_6$ and MC solubility products at solution treatment temperatures above 1150 . Therefore, the carbon content does not cause a difference in $M_{23}C_6$ or MC carbide precipitation. As a result, the content of C was set at 0.10% in view of the room temperature tensile strength and weldability.



Fig. 4 Effect of C content on creep rupture strength

As a result of the development, the chemical composition of the new alloy (AA-1) was determined to be 0.1C-18Cr-10Ni-3Cu-0.25Nb-0.1Ti-0.002B, as shown in **Table 2**. The range of each element can vary as also shown in **Table 2**. The Ni content was increased from that shown in **Table 1** to prevent the formation of – ferrite.

3. Properties of test manufactured tubes

A tube with an outside diameter of 45.0 mm and a thickness of 9 mm was test manufactured from an alloy of the chemical composition shown in **Table 2** to evaluate various properties. Both a shot-blasted internal surface⁶⁾ and a fine-grained internal surface⁷⁾ can be used to reduce the formation of steam oxidation scale on the tube internal surface.

3.1 Mechanical properties

Photo 1 shows the microstructure of the developed steel tube. It may be noted that the microstructure is fully austenitic and does not show -ferrite formation.



Photo 1 Microstructure of developed steel tube

Fig. 5 shows the results of tensile strength tests from room temperature to 800 . No noticeable decline of ductility can be observed over the temperature range.

Fig. 6 shows the results of the creep rupture strength test over a temperature range from 600 to 750. The stress-rupture curves obtained are linear at all temperatures tested within this range and do not indicate any trace of abrupt drop in creep rupture strength.

Fig. 7 shows changes in the Charpy absorbed energy at 0 after long term heating (aging). The test pieces used for this test conformed to the full-sized No. 4 Charpy test piece of the JIS specifications. After 10000 hours aging at 650 , 700 and 750 , the test showed Charpy absorbed energies greater than 80 J, indicating sufficiently good toughness.

Table 2 Chemical compositions of developed steel

											(mass %)
	С	Si	Mn	Р	S	Cu	Ni	Cr	Nb	Ti	В
Sample tube	0.10	0.29	1.57	0.025	0.004	2.87	10.37	17.92	0.27	0.19	0.0024
Range	0.07 - 0.14	1.00	2.00	0.040	0.005	2.50 - 3.50	9.00 - 12.00	17.50 - 19.50	0.10 - 0.40	0.10 - 0.25	0.0010 - 0.0040



Fig. 5 Tensile properties at elevated temperature of developed steel tube



Fig. 6 Creep rupture strength of developed steel tube



Fig. 7 Charpy impact test result after aging

3.2 Allowable stress

Fig. 8 compares allowable stress values for the developed steel at temperatures above 600 obtained by the calculation methods specified in the "Technical Standards for Thermal Power Generating Facilities" using the values obtained for KA SUS321J1HTB steel and TP347HTB steel. At high temperatures above 650 , the developed steel showed allowable stress values that were about 1.4 times and 1.2 times those of TP347HTB steel and KA SUS321J1HTB steel, respectively. The allowable stress of the developed steel at 675 exceeds 58 N/mm², satisfying the target allowable stress of 54 N/mm² for development at that temperature.



3.3 High temperature strength of welding joint

Boiler tubes must have sufficient high temperature strength at the welded joints. NKK has already developed a TIG wire and rod as welding consumables with the chemical composition modeled on the base metal. **Fig. 9** shows the results of creep rupture tests on tube joints welded with these welding materials. It may be noted from the figure that the observed creep rupture strengths of the welded joints are comparable to the mean rupture strengths observed for the base metal at the temperatures tested.



Fig. 9 Creep rupture strength of welded joint of developed steel tube

3.4 Corrosion resistance

The high temperature corrosion properties of the outside surface and the steam oxidation properties of the inside surface of the developed tube were tested to confirm their corrosion resistance as boiler tubes. The high temperature corrosion test was done on test piece coupons, each measuring 10 x 15 x 5 mm, that were cut from the test tube. The test pieces were subjected to high temperature corrosion tests with heavy-oil ash at 600 and 650 for 1000 hours. As a control, SUS321HTB steel with a composition of 17Cr-10Ni-0.4Ti was also used. The results of the high temperature corrosion test are shown in Fig. 10. The developed steel and the control are almost equal in corrosion resistance, because the high temperature corrosion resistance is determined basically by the chromium content in the steel.



Fig. 10 High temperature corrosion test results

The steam oxidation properties were tested at 600 for 1000 hours on three samples: the developed tube, the developed tube with shot-blasted treatment⁶⁾ on the inside surface and SUS321HTB as the control. **Fig. 11** shows the results of the tests. As is the case with the high temperature corrosion resistance test, the developed tube and the control produced about the same amounts of scale, since formation of the steam oxidation scale is dictated by the chromium content in the steel. By sharp contrast, the shot-blasted tube showed excellent resistance to steam oxidation, indicating the possibility that the developed tube can provide the advantage of shot blasting.



4. Discussion

The developed steel tube represents a marked improvement in high temperature strength over KA SUS321J1HTB steel. **Fig. 12** shows the relationship between the amount of precipitated carbides and the solid solution temperature of the developed steel tube. The straight line at 45° represents an atomic ratio of (Ti+Nb) to C of 1:1. Stabilized austenitic stainless steels (SUS347, SUS321) show atomic ratios almost on this line. The area below this line represents excess (Ti+Nb) relative to added C, where the precipitation of $M_{23}C_6$ carbide does not take place.

The developed steel tube contains small amounts of Ti and Nb that place its composition on the upper side of this 45° line. In other words, there would be excess C if all the added (Ti+Nb) combined with C to form MC carbide. Point A represents a steel with 0.1 weight percent of C, 0.18 weight percent of Ti and 0.28 weight percent of Nb. The line representing this steel composition meets the solubility line at Point B if solution treatment is done at 1190 . The amount of C corresponding to (Ay-By) remains as undissolved MC carbide, preventing growth of the grains. The amount of C corresponding to (By-Dy) precipitates as MC car-



Fig. 12 Relationship between amount of precipitated carbides and solid solution temperature

bide during creep, improving the high temperature strength.

Further, the amount of C corresponding to (Dy-0) precipitates as $M_{23}C_6$ carbide, contributing to improvement of creep rupture strength, together with the MC carbide mentioned above. The $M_{23}C_6$ carbide, in particular, contributes to the long-range improvement of creep rupture strength as exemplified by the fact that SUS304H steel has stable long-term creep rupture strength.

As may be noted from **Fig. 6**, the developed steel does not show an abrupt decline of strength in the longterm region at any temperature tested, which may be attributable to the effect of $M_{23}C_6$ carbides. The composition was designed under the following considerations. As a measure against sensitization, the precipitation of $M_{23}C_6$ carbide is held to not more than 0.03 weight percent carbon. Regarding the MC carbide, the atomic ratio of TiC to NbC is designed to be unity to maximize creep rupture strength. In addition to precipitation strengthening by these carbides, the precipitation strengthening of 3 weight percent copper additions alone contributes to the high temperature strength of this alloy, as shown in **Fig. 8**.

Photo 2 shows a representative example of Cu-rich phase precipitation observed by TEM (Transmission Electron Microscopy). **Photo 3** shows $M_{23}C_6$ and MC carbide precipitation. Very fine Cu-rich phase and MC carbide particles measuring not more than 0.1 μ m and dispersed fine precipitates measuring about 0.2 μ m can be observed. This shows that these fine dispersed precipitates increase the creep rupture strength of the developed alloy.

5. Conclusion

NKK recently developed TEMPALOY AA-1, an austenitic stainless tube with superior high temperature strength for USC (Ultra Supercritical) thermal power plants. Evaluation of the results of various property tests of the manufactured prototype tube lead to the following conclusions.



Photo 2 TEM observation result of Cu-rich phase precipitation (650 , 3800 h ruptured specimen)



Photo 3 TEM observation result of carbide precipitation (700 , 3600 h ruptured specimen)

(1) The basic composition is 18Cr-10Ni austenitic stainless steel, to which trace amounts of Ti, Nb and 3 weight percent of Cu are added.

(2) This new stainless steel has a creep rupture strength about 1.4 times greater than that of TP347HTB. This tube alone can be used in the severe steam conditions exceeding 630 and 30 MPa that are forecast for the future.

(3) The high temperature strength of this developed tube may be attributable to the presence of a Cu-rich phase and to the precipitation strengthening of MC and $M_{23}C_6$ carbides.

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