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Development of New Austenitic Stainless Steel Boiler Tube with High Strength at Elevated Temperatures and Intergranular Corrosion Resistance

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Abstract

A new austenitic stainless steel boiler tube, low C-18Cr-9Ni-Nb-V-W-N (XA704), has been developed. The high temperature strength and the intergranular corrosion resistance of XA704 are superior to those of conventional tubes such as type 347H (JIS SUS347HTB). This excellent creep strength of XA704 is mainly due to precipitation strengthening by CrVN, and solid solution strengthening by tungsten and nitrogen. The result of the field test for 2 years indicated that XA704 would maintain its performance over a long period of time. Thus XA704 is suitable for use as a material for superheater and reheater tubes of thermal power boilers.

1. Introduction

Superheaters and reheaters are operated at the highest temperature range among the pressure parts of thermal power boilers. Therefore, it is essential for steel tubes for this kind of application to have high strength and corrosion resistance at elevated temperatures. For this reason, austenitic stainless steel tubes have been used as the main material for this type of equipment. For application to an ultra-super-critical boiler (USC boiler), Nippon Steel Corporation has developed NF709[1)] (KA SUS310J2TB), a steel having significantly better strength and corrosion resistance at elevated temperatures than JIS SUS347HTB. However, since the basic chemical composition of NF709 was 20Cr-25Ni, material costs were inevitably higher than those of 18Cr-8Ni stainless steels. When the steel was used for conventional super- or sub-critical boilers, the advantage of its high strength could not be fully applied.

Some kind of 18Cr-8Ni stainless steels boiler tubes with high strength have been developed recently in consideration of material costs. However, although these steels had a high carbon (C) content to realize high strength, none of them contained C-stabilizing elements such as Nb and Ti in amounts sufficient for the high C content. Consequently, Cr carbide easily precipitated at grain boundaries and Cr-depleted layers formed near the boundaries. For this reason, the developed boiler tube steels had a high sensitivity (easily sensitized) to intergranular corrosion[2)]. Therefore, when a boiler tube of such a steel was welded to another boiler tube of a high-strength ferritic stainless steel, typically such as KA STBA29, the austenitic material sensitized during a post-welding heat treatment (PWHT) required for the ferritic material, and as a result, intergranular cracks sometimes developed before the boiler was put into operation.

It has been necessary, as a countermeasure against the above, to take troublesome processes such as to apply protective painting to welding heat-affected zones or to weld an austenitic material such as SUS347HTB, which does not easily sensitize, to the high-strength ferritic material, apply a PWHT and then weld a high-strength austenitic material[3)].

In view of the above, Nippon Steel has newly developed an austenitic stainless steel boiler tube, XA704 (KA SUS347J1TB)[4-7)]. The

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steel was developed on the basis of the chemical composition of an 18Cr-8Ni system in consideration of economical efficiency, and had a low C content for securing good resistance to intergranular corrosion. Despite the low C content, a higher strength at elevated temperatures than that of the conventional steels was attained for the same application. The design concept of the chemical composition of XA704, its properties and actual applications are presented below.

2. Guidelines for Chemical Composition Design of XA704

A steam temperature of 600°C (a metal temperature of 650°C) was selected in defining the use condition of the new steel tube product. According to the targets set forth for the chemical composition design of XA704 under the above temperature condition, the maximum allowable stress had to be significantly higher than that of conventional SUS347HTB, and resistance to the corrosion and steam oxidation at high temperatures and resistance to intergranular corrosion had to be at the same level as those of the steel. **Fig. 1** schematically illustrates the guidelines for the chemical composition design of XA704.

For the purpose of reducing alloy costs and securing the same level of resistance to the corrosion and steam oxidation at elevated temperatures as those of conventional steels, an 18Cr-9Ni system was selected as the basic chemical composition of the new steel. In addition, in order to realize good resistance to intergranular corrosion, the C content was set as low as 0.03% approximately[2)].

The difficulty in the development of XA704 lied in how to make up for low creep strength resulting from the low C content. It is often the case with the latest high-strength austenitic stainless steel tubes, typically such as NF709, that high strength is achieved by controlling the C content to 0.07 to 0.10% and realizing precipitation strengthening using NbC and CrNbN (Z phase). In the development of XA704, the content of N, instead of that of C, was set rather high at 0.2% so as to realize as much precipitation strengthening as possible and to obtain an effect of solution strengthening as well. With respect to Nb, unless the temperature of solution heat treatment is high enough, its addition by a large amount results only in an increase in coarse insoluble Nb precipitate, and does not contribute to enhancing strength. In the case of a high-N system like XA704, the practical upper limit of solution heat treatment temperature is 1,250°C. In this temperature range, an addition of Nb by 0.3% or more does not result in any significant increase in strength, as seen in **Fig. 2**.

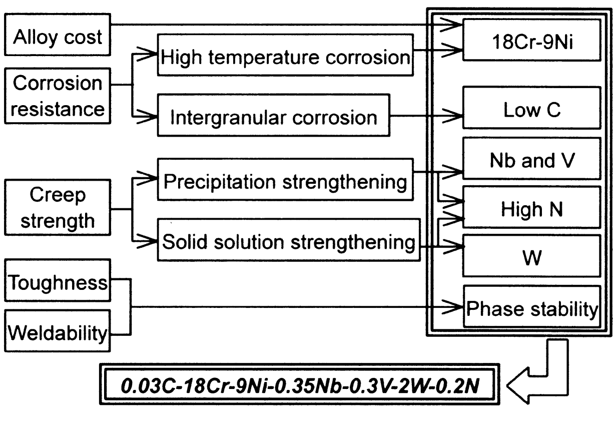

Fig. 1 Alloy design concept of XA704

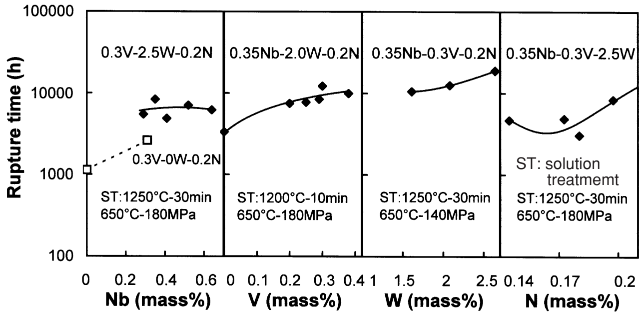

Fig. 2 Effect of Nb, V, W and N on creep rupture time for 0.03C-18Cr-9Ni steel

In view of the above, for the purpose of improving steel strength yet further, the authors investigated the effects of various alloying elements, and as a result, found out that addition of V was effective. V was not added to conventional austenitic stainless steels for boiler tubes except for Esshete1250[8)]. This was because as far as the above kind of steel for boiler tubes having a high C content was concerned, V was not considered to be effective in maintaining high strength for a long period of time, because it precipitated in the form of carbide and the precipitates coagulated to form coarse particles within a comparatively short period[9)]. However, as a result of the analysis of the precipitates for the purpose of clarifying the strengthening mechanism, the authors have confirmed the following: In a low-C and high-N system like XA704, V precipitates in the form of strings of nitrides; in a long period of time, fine particles of CrVN (Z phase) disperse in steel in a high density, without coagulating inside grains into coarse particles; thus V has a high ability of precipitation strengthening[4-7)] (see **Fig. 3**).

In a system to which V and Nb are added in combination, the precipitate consists mainly of CrVN, and Nb is caught in the precipitate. CrVN precipitates in fine particles in a high density just as CrNbN does, which was used in NF709 for precipitation strengthening, and the former is expected to have a strengthening effect equal to or greater than that of the latter. The advantage of V over Nb is that V can be made solute in a greater quantity at a lower heat treatment temperature than Nb is. Therefore, the strengthening effect due to the precipitation of the solute V that occurs during the use of the tube can be enjoyed to the fullest extent. It should be noted that although there were fears, proved needless later, that V would lead to V attack, the authors have confirmed that V does not cause any V attack as far as its content is 0.5% or less[6)]. In order to further strengthen steel, W was added as another solution-strengthening element. Fig. 2 shows the effects of the addition of elements on the

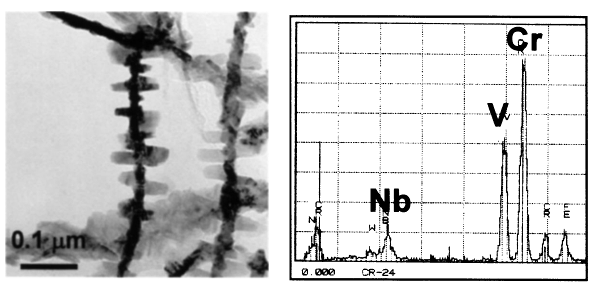

Fig. 3 Precipitates of XA704 after the field test at 600°C for 16,000 h

Table 1 Specified chemical composition of XA704 and an example

(mass%)

C	Si	Mn	Ni	Cr	Nb	V	W	N
0.05 max	1.00 max	2.00 max	8.0 - 11.0	17.0 - 20.0	0.25 - 0.50	0.20 - 0.50	1.5 - 2.6	0.10 - 0.25
0.03	0.27	1.69	9.85	18.45	0.37	0.30	2.13	0.23

creep rupture time in a comparatively long time span. It is shown here that V, W and N are effective in enhancing creep rupture strength.

The specified chemical composition of XA704 was defined as shown in **Table 1** in consideration of prevention of toughness deterioration in a long run, securement of steam oxidation resistance, enhancement of weldability and so forth, in addition to the above strengthening measures.

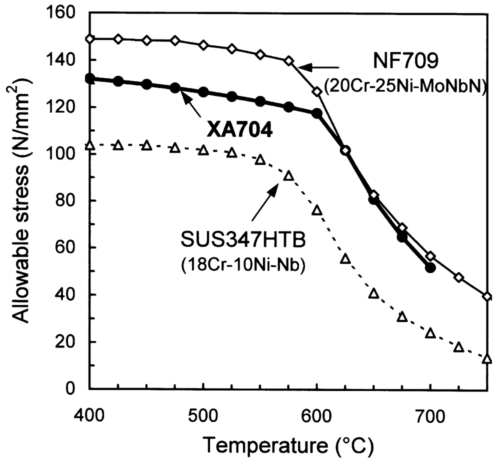

Fig. 5 Maximum allowable stress of XA704

3. Properties of Developed Steel Tube

3.1 Creep rupture properties and maximum allowable stress

Fig. 4 shows the results of creep rupture tests with XA704 steel tube produced on commercial production facilities (mill tube) and steel plate prepared by laboratory- melting and rolling process. According to creep rupture data for periods longer than 50,000 h obtained so far, the relationship between stress and rupture time is substantially linear, and no drastic fall of rupture stress in a long run has been observed. Using the data of Fig. 4, the authors have estimated the creep rupture strength of XA704 by the Larson-Miller analysis method. The result obtained was 121 N/mm^2 under the condition of 650°C and 100,000 h, substantially the same as that of NF709 (KA SUS310J2TB) under the same temperature-time condition. **Fig. 5** shows the maximum allowable stresses of XA704 calculated from the above test results compared with those of NF709 and SUS347HTB. The maximum allowable stress of XA704 is higher than that of SUS347HTB by approximately 30 N/mm^2 at different temperatures, and is nearly equal to that of KA SUS310J2TB at 625 and 650°C. The maximum allowable stress mentioned above is the value of the standard allowable stress of XA704 that was approved when the steel was newly standardized in the METI (Japanese Ministry of Economy, Trade and Industry) Code under the denomination of KA SUS347J1TB in 2002.

3.2 Corrosion resistance

Excellent intergranular corrosion resistance of XA704, which was one of the targets envisaged in its development, has been confirmed through the Strauss test (ASTM A262 Practice E). **Fig. 6** compares XA704, SUS304HTB, SUS347HTB and NF709 in terms of the intergranular crack sensitivity after a heat treatment under the conditions of 550 to 850°C and 0.1 to 1,000 h. XA704, SUS347HTB, NF709 and SUS304HTB showed good intergranular corrosion resistance in this order, and no intergranular crack whatsoever occurred to XA704 under the above condition ranges. From these results, XA704 is considered to be less prone to sensitizing to intergranular cracking than SUS347HTB is, which has been deemed to be little prone to sensitizing to it.

Comparative specimens were prepared by melting steel according to the same chemical composition as that of KA SUS304J1HTB (0.10C-18Cr-9Ni-0.4Nb-Cu), a typical steel among conventional high-strength and high-C steels for thermal power boiler use, and then rolling into plates on laboratory equipment. The comparative specimens thus prepared were submitted, together with specimens of XA704, to sensitization under the condition of 650°C × 2 h + air cooling and then a Strauss test. The occurrence of cracks to the specimens at the test is shown in **Fig. 7**. It is clear from the photographs that the intergranular corrosion sensitivity of XA704 is by far the lower than that of the 0.10C-18Cr-9Ni-0.4Nb-Cu steel.

Next, the corrosion resistance of XA704 at elevated tempera-

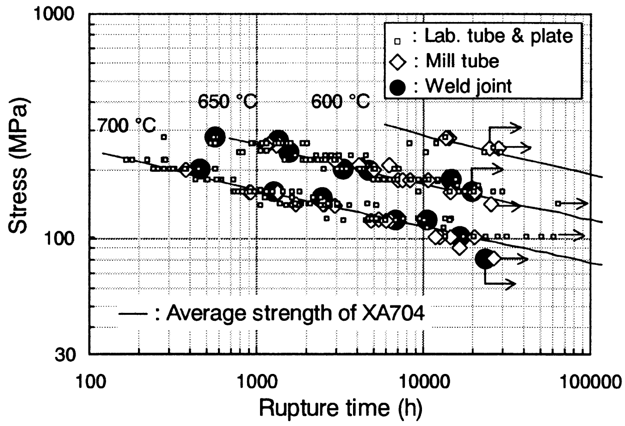

Fig. 4 Creep rupture strength of XA704

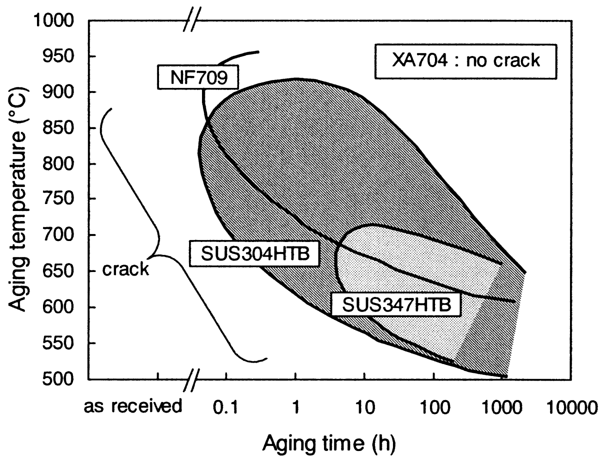

Fig. 6 Results of intergranular corrosion test of aged tubes

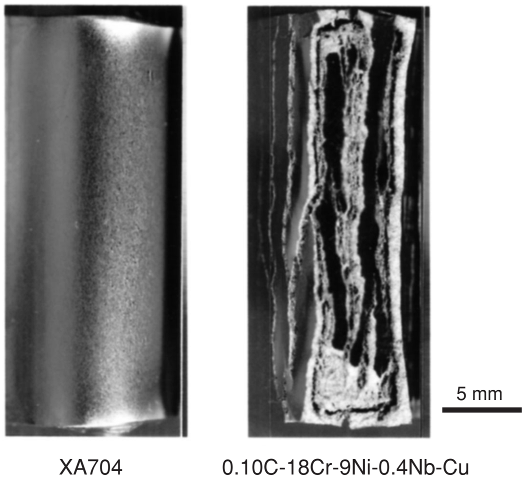

Fig. 7 Appearance of bent specimens after intergranular corrosion tests

tures was examined. **Fig. 8** shows the results of a test simulating the hot corrosion of tube outer surfaces at high temperatures caused by coal ash, and **Fig. 9** those of a steam oxidation test simulating the environment of tube inner surfaces. It is clear from the graphs that XA704 has substantially the same resistance to the coal ash corrosion and steam oxidation at high temperatures as that of SUS347HTB.

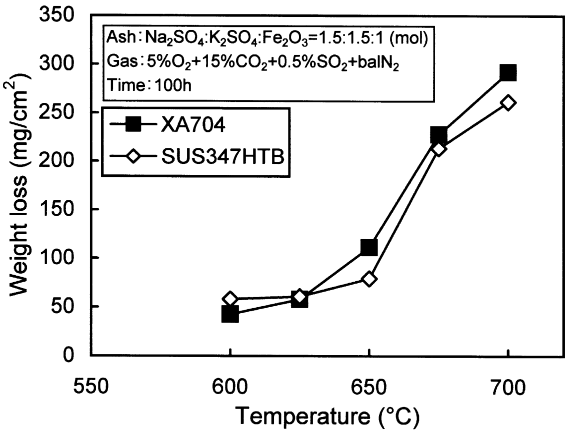

Fig. 8 Hot corrosion resistance of XA704

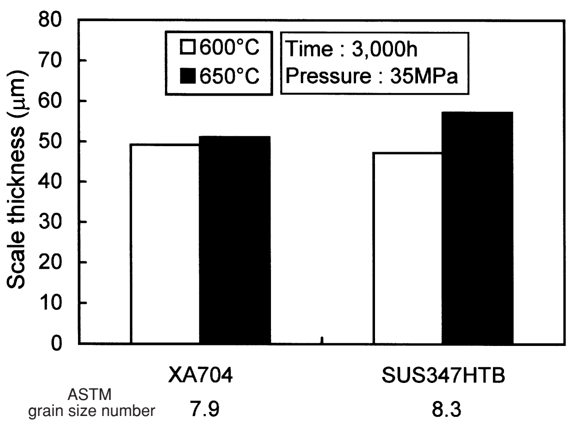

Fig. 9 Steam oxidation resistance of XA704

This is presumably because the two steels are nearly the same in terms of Cr content and grain size.

3.3 Toughness after aging

Fig. 10 shows the Charpy impact test results of XA704 aged at 600°C, 650°C and 700°C for up to 10,000 h. As seen generally with austenitic heat-resistant steels, the longer the aging time, the lower the Charpy impact values became. However, XA704 maintained a sufficiently good toughness for boiler tube application even after the aging at 700°C for 10,000 h.

3.4 Weldability and welding consumables

For the purpose of evaluating the hot cracking susceptibility of XA704, a Varestraint test was carried out using specimens of commercially available JIS SUS304 and SUS310S as comparative materials. The results are shown in **Fig. 11**. It is clear from the graph that, as a result of the alloy design of XA704 to optimize the amount of δ ferrite in the solidification structure, its hot cracking sensitivity is lower than that of SUS304. Additionally, matching welding consumables of gas tungsten arc welding (GTAW) and shielded metal arc welding (SMAW) for XA704 have been developed. As is shown in Fig. 4, the creep rupture strength of weld joints is equal to that of the base metal.

4. Actual Application

XA704 steel tubes were tested as the superheater tubes of Tokai No. 7 boiler of Nippon Steel Nagoya Works for about 2 years. The authors confirmed, as a result of their examination after removing from the equipment, that the material had little deteriorated, and thus

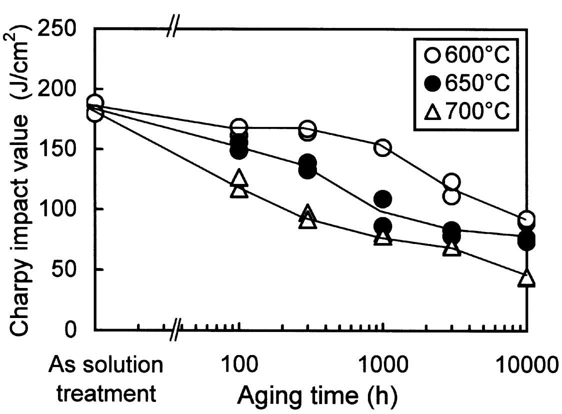

Fig. 10 Charge in Charpy impact value at 0°C after aging

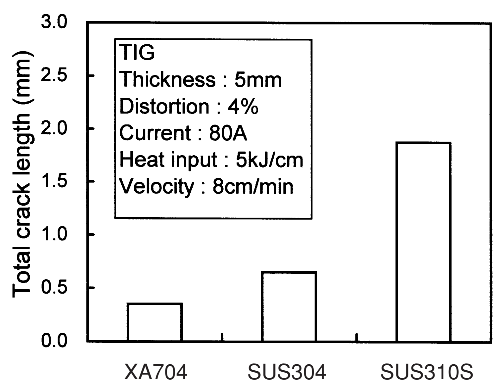

Fig. 11 Results of Varestraint test

the product proved to be well applicable to long-term use[5]. Based on the above results, XA704 was standardized in the METI Code. Thus, the condition has been provided for wide application of the XA704 steel tubes to power boilers in Japan. The XA704 tubes have been commercially applied to No. 9 power station of Nippon Steel's Oita Works and other three power plants, and the total shipment of the product has reached approximately 250 t. In order to make the steel applicable to overseas power boilers, Nippon Steel is making preparations for the registration of the steel with the ASME and ASTM standards.

5. Closing

As has been explained above, the XA704 steel tube is a boiler tube product having an excellent strength at high temperatures and good workability, despite its chemical composition of an economical 18Cr-8Ni system. Now that the product has been included in the METI Code, its use as the superheater and reheater tubes of a super- or sub-critical boiler is expected to expand.

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