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Development of Boiler Tubes and Pipes for Advanced USC Power Plants

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Abstract

Development of advanced-USC (A-USC) boiler technology has been promoted in recent years, which features 700°C steam condition. HR6W and HR35, which can be applied for A-USC boilers, have been developed on the basis of unique alloy design; that is, these alloys employ precipitation strengthening of Laves and/or α-Cr phases without γ' phase. The 10^5 h average creep rupture strength of HR6W at 700°C is 85 MPa. Excellent creep rupture ductility and microstructural stability have been revealed even in the long-term creep deformation. Furthermore, it has also been clarified that they have superior creep-fatigue strength and high resistance to stress-relaxation cracking compared with γ' hardened Alloy 617. The 10^5 h average creep rupture strength of HR35 at 700°C is comparable with Alloy 617. It indicates that HR35 can be applied for main steam thick-wall pipes in A-USC boilers.

1. Introduction

In recent years, boilers for coal-fired power plants have been constructed at a rapid pace in China, India and other newly industrializing economies. In Japan, too, the importance of boilers for thermal power generation has continued to grow ever since the country's use of nuclear power dropped in the wake of the 2011 Great East Japan Earthquake and tsunami waves. However, in terms of unit of electrical energy generated, coal-fired power generation emits more CO_2 than any other type of power generation. From the standpoint of suppressing global warming, it is extremely important to improve coal-fired power generation efficiency. In the 1990s, Japan was the first country in the world to put into practical use a high-efficiency, ultra-super-critical (USC) boiler (steam temperature: 600°C class) for coal-fired power plants.[1)] Recent years have seen the development of advanced ultra-super-critical (A-USC) boiler technology that is aimed at raising steam temperature to 700°C.[2, 3)] The key to ensuring more favorable steam conditions is the development of new boiler tubes and pipes for use under more severe high-temperature environments.

Nippon Steel & Sumitomo Metal Corporation has developed boiler tubes and pipes that are marketed as SUPER304H®, SUS304J1HTB, ASME SA213 Code Case (CC) 2328 and TP347HFG (ASME SA213 TP347HFG), which have become world standard,[4)] and in this way the company has contributed much to the development of USC boilers. It is also pressing ahead with the development and commercialization of the high-strength Ni-based alloys HR6W (ASME SB167 CC 2684) and HR35, which are suitable for A-USC boilers.[5)] The company is working with Japanese manufacturers of boilers, turbines, and valves in a nine-year (FY 2008–FY 2016) project named "Development of Component Technologies for the Practical Application of Advanced USC Thermal Power Generation," which is subsidized by Japan's Ministry of Economy, Trade and Industry (METI). Project members have been striving to evaluate the long-time properties of the abovementioned newly developed alloys and to establish the application technology. The project members plan to conduct a series of boiler component tests using 700°C steam.[6, 7)] This report describes the alloy design, microstructure, strength, and other properties of HR6W and HR35 evaluated in the METI project.

2. Development of Ni-Based Alloys for A-USC Boiler Pipes and Tubes

2.1 HR6W

2.1.1 Alloy design

When developing HR6W for A-USC boiler pipes and tubes, importance was attached to not only its creep rupture strength but also

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Table 1 Chemical requirements of HR6W tubes and pipes for ASME standards

(mass%)

C	Si	Mn	Cr	Fe	W	Ti	Nb	B	N	Ni
≦ 0.10	≦ 1.0	≦ 1.50	21.5 - 24.5	20.0 - 27.0	6.0 - 8.0	0.05 - 0.20	0.10 - 0.35	0.0005 - 0.006	≦ 0.02	Remainder

Photo 1 TEM microstructure of extracted replica of HR6W aged at 750°C for 3,000 h

its creep ductility, thermal fatigue resistance, and fabricability into large-diameter, thick-walled pipes. The precipitation strengthening of γ'-phase (Ni_3 (Al, Ti)) used for conventional high-strength Ni-based alloys was not applied in the design of the new alloy.

First, from the standpoint of corrosion resistance and microstructural stability for use in 700°C class A-USC boilers, the optimum amount of Cr was decided to be 23%. The creep rupture strength and microstructure of Ni-Fe-Mo-W model alloys were studied.[8] When Mo was added singly, σ phase (an embrittlement phase) precipitated in large quantities during more than 10,000 hours of creeping at 700°C to 750°C, causing strength, creep ductility, and thermal fatigue resistance to deteriorate markedly. On the other hand, when only W was added, it was possible to restrain the precipitation of σ phase during the many hours of creeping and obtain a stable microstructure with an optimum Ni content of 45%. In addition, from the results of phase diagram calculations and experiments it was confirmed that a comparatively fine Laves phase of Fe_2W type precipitated during creeping, helping to strengthen the alloy significantly.

The optimum composition of the ultimately developed alloy HR6W was established as 23Cr-45Ni-7W.[9-11] **Table 1** shows the composition specifications of HR6W registered in the ASME Standard. In addition to W, the alloy is added with C, Ti, Nb and B to increase alloy strength through the formation of fine carbides.

Photo 1 shows the microstructure of an extracted replica of HR6W aged at 750°C for 3,000 h. Even after these many hours of aging, the microstructure reveals a fine Laves phase and $M_{23}C_6$ carbide, and is free of σ phase precipitation. **Figure 1** shows the phase fractions of HR6W calculated using the Thermo-Calc. Even at 800°C, the Laves phase precipitates stably, indicating that it helps strengthen the alloy in the temperature region in which it would be used for A-USC boilers.

2.1.2 Creep rupture strength and microstructure

Figure 2 shows the creep rupture strength of HR6W. Including creep rupture data collected over a maximum period of more than 60,000 hours, the stress-creep rupture diagrams show a mild gradient, demonstrating that the alloy maintains high creep rupture strength on a stable basis even in a temperature range of 650°C to 800°C. The average creep rupture strength of HR6W for 100,000

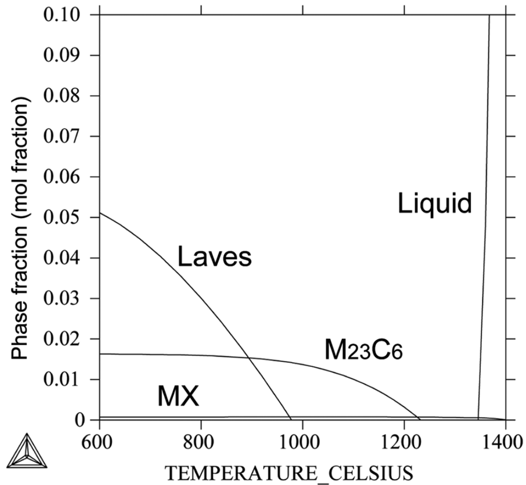

Fig. 1 Phase fractions of HR6W computed by Thermo-Calc

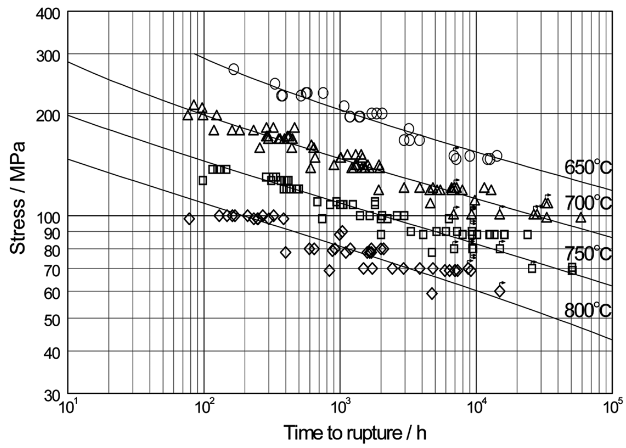

Fig. 2 Creep rupture strength of HR6W

hours registered in the German Standard TUV (VdTUV559/2) is 118 MPa at 650°C, 85 MPa at 700°C, 62 MPa at 750°C, and 42 MPa at 800°C. It has been confirmed that HR6W also has good creep rupture ductility even on the long-hour side.[11]

Photo 2 shows an optical micrograph (longitudinal section of specimen) of HR6W ruptured at 700°C, 98 MPa, in 58,798 h. Many precipitates were observed at the grain boundaries and in the grains. Those precipitates were mainly Cr-based carbides (identified later as $M_{23}C_6$ under TEM). Blocky embrittlement phases, such as the σ phase, were not observed at all. The creep rupture elongation of the above-mentioned ruptured specimen was 39%, while the microstructure in the neighborhood of the ruptured part revealed markedly deformed grains. **Photo 3** shows the microstructure of an extracted replica of the ruptured specimen observed under the TEM. The precipitates in grain boundaries were identified as $M_{23}C_6$, while those in

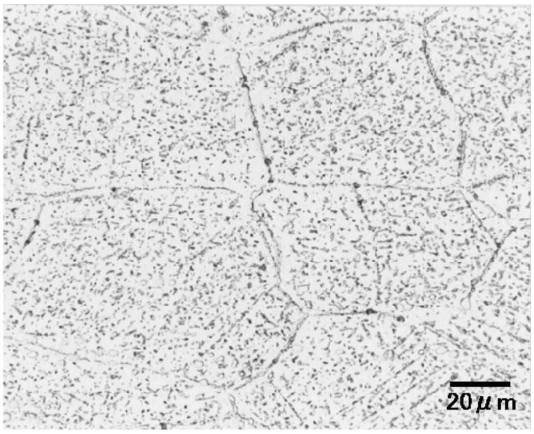

Photo 2 Optical microstructure of HR6W after creep rupture (700°C, 98 MPa, 58,798 h)

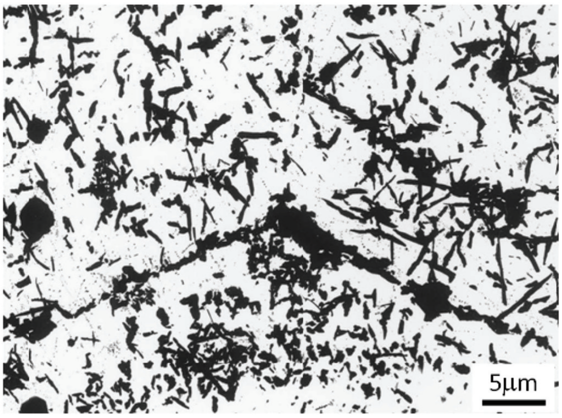

Photo 3 TEM microstructure of extracted replica of HR6W after creep rupture (700°C, 98 MPa, 58,798 h)

grains were identified as Laves phase and $M_{23}C_6$, as shown in Photo 1. Even at 700°C on the long-time side, σ phase was not observed. Precipitates approximately 1 to 3 μm observed in large quantities in the grains were identified as Laves phase (see Photo 3). Extreme coarsening of the Laves phase was not observed. The Laves phase containing W (Fe_2W) gradually precipitates finely with the lapse of time, and takes many hours until precipitation equilibrium is reached. It is estimated that the fine precipitation of the Laves phase over many hours [12] contributes to stable precipitation strengthening of the alloy.

2.1.3 Service performance

Figure 3 compares the creep fatigue strength of HR6W at 700°C with that of Alloy 617 (a general-purpose Ni-based alloy).[13] With regard to CP waveform (0.01%/s on the low-speed (C) side, 0.8%/s on the high-speed (P) side), the creep fatigue life of HR6W is longer than that of Alloy 617. It is widely known that the creep fatigue life of CP waveform has some correlation with creep rupture ductility.[14] Since HR6W has high creep rupture ductility, it is estimated that the alloy shows good creep fatigue resistance. The figure shows SEM images of the fracture surfaces of the two alloys after a creep fatigue test. While Alloy 617 revealed intergranular fractures over the entire surface, HR6W showed many transgranular fractures. The implication is that the fracture ductility of HR6W is higher than that of Alloy 617, and is therefore superior in creep fatigue resistance.

With high-strength Ni-based alloys of the γ'-phase strengthened type, as represented by Alloy 617, stress relaxation cracking (SR cracking) has become a problem. It occurs in the process of relieving welding residual stress while the alloy is used under high temperatures.[15] Sensitivity to SR cracking has much to do with material ductility at high temperatures, when stress relieving occurs easily. In a JIS-compatible hot tensile test (strain rate after yielding: about $1.25 \times 10^{-3}s^{-1}$), Alloy 617 showed good ductility comparable to that of HR6W. In order to simulate the hot deformation at a low strain rate, during which SR cracking occurs, the author and collaborators carried out an extra-low strain rate tensile test, with the strain rate set at $1.0 \times 10^{-6}s^{-1}$, or 1/1000 of the ordinary strain rate.

The test results are shown in **Fig. 4**.[16] In a temperature range of 700°C to 750°C, with A-USC boiler pipes used, HR6W displays

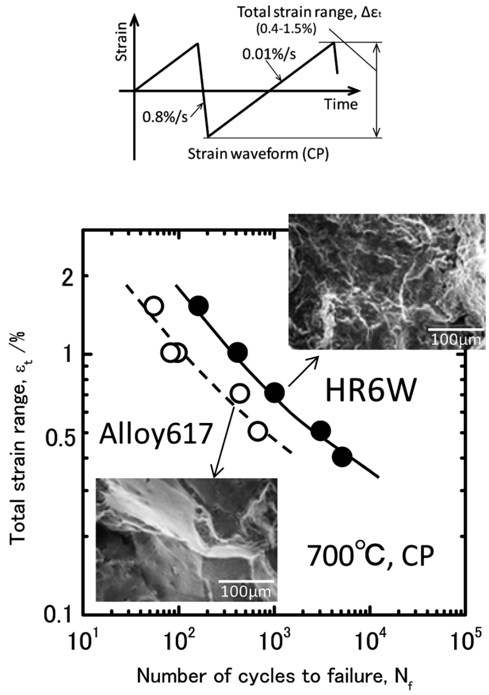

Fig. 3 Creep-fatigue properties of HR6W and Alloy 617 [13]

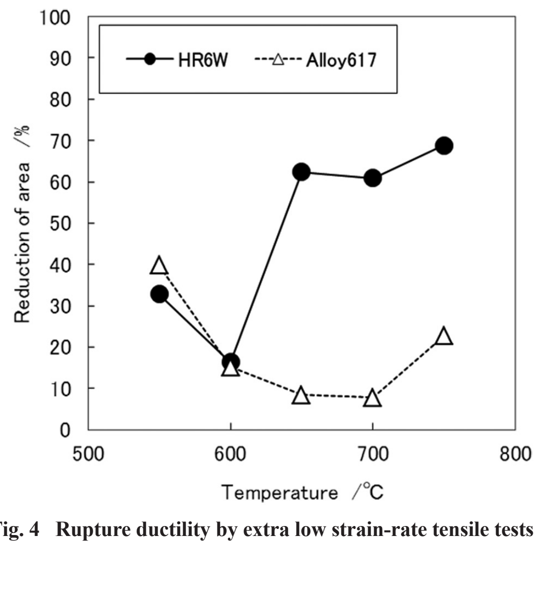

Fig. 4 Rupture ductility by extra low strain-rate tensile tests [16]

high rupture ductility. Next, in order to evaluate the sensitivity of HR6W to SR cracking, the author and collaborators welded for restraint a small-diameter tube whose grain size was adjusted to the same size as that of a large-diameter, thick-walled pipe, subjected the welded pipe to aging at 700°C for 1,000 h, and observed cross sections near the weld zone under an optical microscope.[16] HR6W revealed no SR cracking. In contrast, Alloy 617 showed marked SR cracking. From these results it was judged that the alloy ductility, measured during the above-mentioned extra-low strain rate tensile test, had high correlation with alloy sensitivity to SR cracking. Thus, the test demonstrated that HR6W had excellent resistance to SR cracking.

Figure 5 shows the results of a high-temperature (650°C) corrosion test carried out using synthetic coal ash. It can be seen that HR6W is nearly equal in corrosion resistance to HR3C (25Cr-20-Ni-Nb-N), which is widely used for boiler tubes.

The newly developed HR6W has good hot workability.[17] Large-diameter, thick-walled HR6W pipes of practical sizes have already been test-manufactured to verify the fabricability of HR6W pipes and tubes. **Photo 4** shows an example of a test-made HR6W pipe. The large-diameter, thick-walled HR6W pipe shown was used for a mockup of a reheater header fabricated for the METI project in Japan that was mentioned earlier.

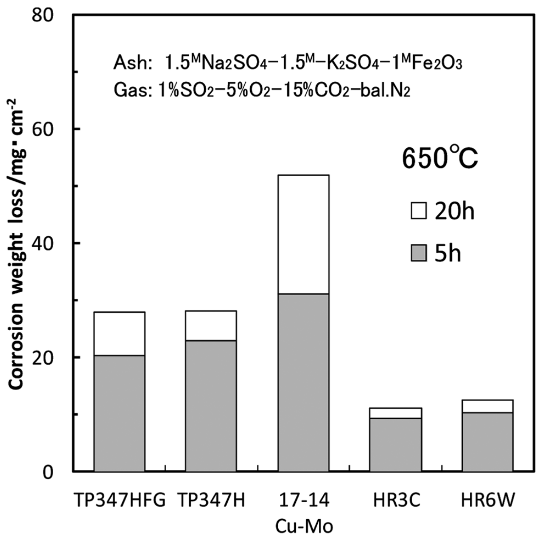

Fig. 5 High temperature corrosion properties of HR6W and other austenitic steels

Photo 4 Appearance of HR6W thick-wall pipe

2.2 HR35

2.2.1 Alloy design

For the main steam pipe of an A-USC boiler, a material superior to HR6W in high temperature strength is required. In order to impart to good ductility, thermal fatigue resistance and formability comparable with those of HR6W for large-diameter, thick-walled boiler pipes, the author and collaborators designed a high-strength Ni-based alloy without applying the precipitation strengthening of the γ' phase.[18] **Figure 6** shows an isothermal section of a Cr-Ni-Fe-7W pseudo-quaternary system at 750°C obtained using the Thermo-Calc. When the Cr and Ni content of HR6W (23Cr-45Ni) are increased further, the α-Cr phase (fine precipitate) stabilizes in addition to the fine Laves phase precipitation. The newly developed HR35 has a base composition of 30Cr-50Ni, and utilizes the α-Cr phase as the main strengthening phase, which is finely precipitated during creeping. In addition, HR35 is added with 4%-6%W and 0.8%Ti to utilize the precipitation strengthening of fine Ni_3Ti as well as the α-Cr phase, Laves phase, and $M_{23}C_6$ carbide.

Photo 5 shows the microstructure of an extracted replica of an HR35 creep-ruptured grip part (750°C, 127 MPa, 2,527 h) observed under a TEM. The rod-shaped precipitates are the α-Cr phase, which has uniformly precipitated finely and densely in the grains. An example of composition analysis using energy dispersive X-ray (EDX) spectroscopy is also shown in the photo. It was found that the α-Cr phase of HR35 contains small amounts of solid solutions of Ni and W.

2.2.2 Creep rupture strength, microstructure, and other properties

Figure 7 shows the creep rupture strength of HR35. For HR35, creep rupture data for over a maximum of 20,000 hours has already been accumulated, and the results of a long-time test are being evaluated. The average creep rupture strength of Alloy 617 at 700°C (source: ECCC data sheet) is shown by the dotted line in the figure. The 100,000-hour average creep rupture strength of HR35 at 700°C is considered to be equal or superior to that of Alloy 617. In addition, the gradient of the stress-rupture time curve of HR35 is mild, showing that HR35 has stable creep rupture strength even on the long-time side at 700°C to 800°C. Furthermore, it has been confirmed that the creep rupture ductility of HR35 on the long-time side is quite satisfactory.[18]

Photo 6 shows an optical micrograph of a longtime creep rupture specimen of HR35 (700°C, 157 MPa, 13,110 h). HR35 showed good microstructural stability without precipitation of the σ-phase

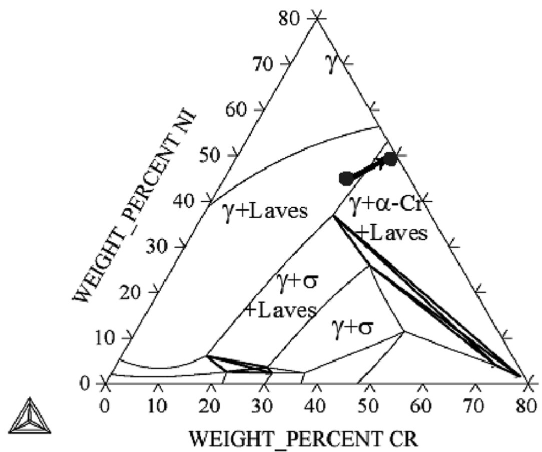

Fig. 6 Calculated phase diagram of Cr-Ni-Fe-7W system (750°C)

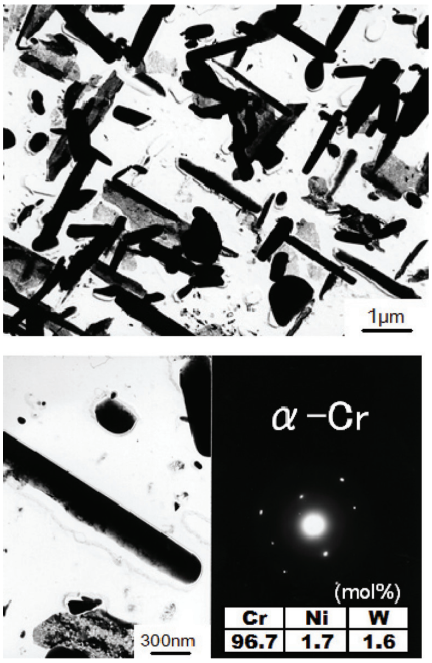

Photo 5 TEM microstructures of extracted replica of HR35 after creep rupture (750°C, 127 MPa, 2,527 h)

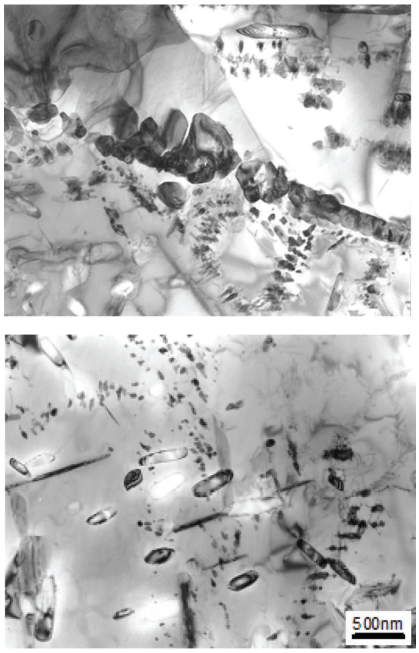

Photo 7 TEM microstructures of HR35 after creep rupture (700°C, 157 MPa, 13,110 h)

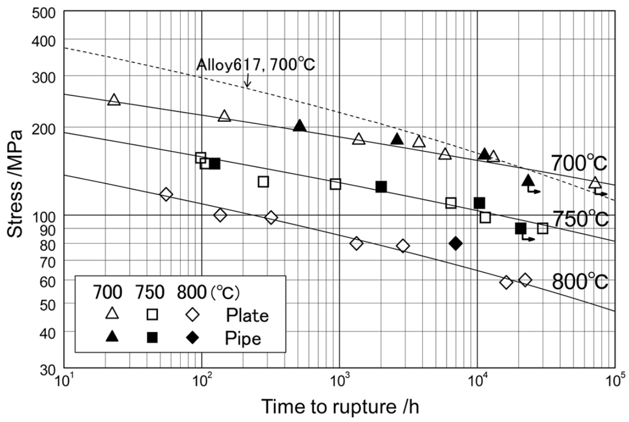

Fig. 7 Creep rupture strength of HR35

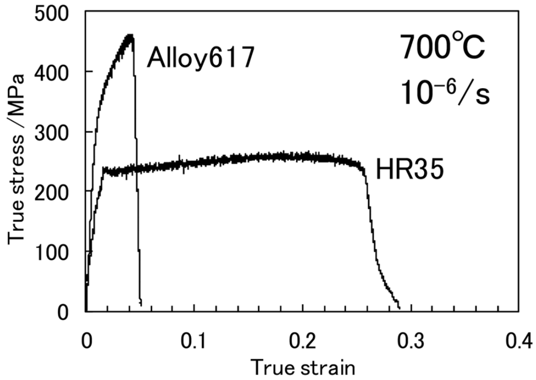

Fig. 8 S-S curves obtained by extra low strain-rate tensile tests

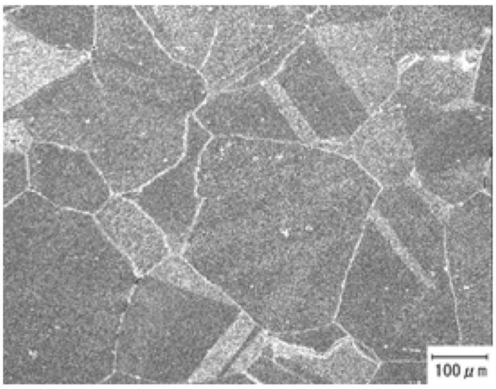

Photo 6 Optical microstructure of HR35 after creep rupture (700°C, 157 MPa, 13,110 h)

and any other embrittlement phase. **Photo 7** contains thin-film TEM micrographs of a ruptured specimen of HR35 (upper photo: intergranular; lower photo: transgranular). From these results, and the results of SEM observations, it was found that the grain boundaries were densely covered with precipitates that were mostly identified as $M_{23}C_6$ carbide. Rod-shaped precipitates in the grains were the α-Cr phase, and marked coarsening of the phase was not observed.

Next, in order to evaluate sensitivity to SR cracking, the author and collaborators carried out an extra-low strain rate tensile test with the strain rate set at $1.0 \times 10^{-6}s^{-1}$, and evaluated the rupture ductility of HR35. The stress-strain curve at 700°C is shown in **Fig. 8**, while rupture ductility at 600°C to 800°C is shown in **Fig. 9**. A marked difference in hot tensile ductility was observed between HR35 and Alloy 617. Compared with Alloy 617, HR35 has much higher ductility, and is considered to have good resistance to SR cracking.

The hot workability of HR35 is better than that of Alloy 617. A large-diameter, thick-walled HR35 pipe (350 mm in diameter, 40 mm in wall thickness) was successfully manufactured and evaluated (**Photo 8**). It was confirmed that the creep rupture strength of the

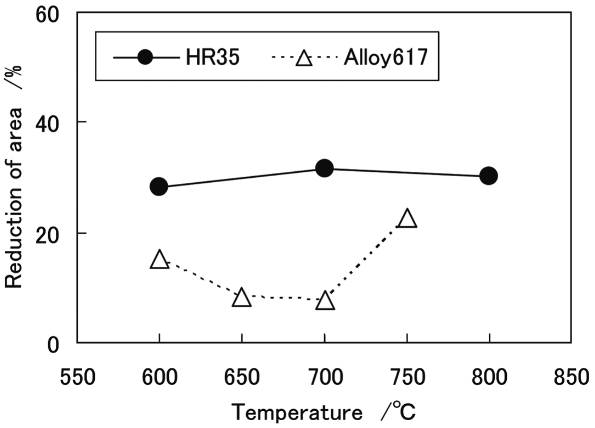

Fig. 9 Rupture ductility by extra low strain-rate tensile tests

Photo 8 Appearance of HR35 thick-wall pipe

large-diameter pipe shown in Fig. 7 was nearly equal to that of the HR35 plate manufactured in the laboratory. The longtime creep rupture strength of HR35 is being evaluated.

3. Evaluation of HR6W and HR35 in the METI Project

Nippon Steel & Sumitomo Metal has been pressing ahead with research on the practical use of alloy pipes and tubes for A-USC boilers as part of its participation in the project entitled "Development of Component Technologies for Practical Application of Advanced USC Thermal Power Generation," subsidized by Japan's METI. The first five years, from FY 2008 to FY 2012, were devoted to the development of the component technologies. For common test materials, including HR6W and HR35, the company is responsible for the project's focus on the properties of the base metals, while the boiler manufacturers are responsible for its focus on the properties of the joints. For HR6W and HR35, the companies have carried out various evaluation tests for the base metals and welded joints (using the general purpose welding material for Alloy 617) of plates, large-diameter thick-walled pipes, and small-diameter tubes. Both the base metals and the welded joints demonstrate excellent properties for practical uses.[19]

4. Conclusion

Nippon Steel & Sumitomo Metal has developed HR6W (ASME SB167 CC 2684) and HR35 as high-strength Ni-based alloys for 700°C class A-USC steam boilers. This report describes the alloy designs, creep rupture strengths, microstructures, and service performances of those alloys. It is expected that the new alloys will contribute much to the realization of the world's first 700°C class A-USC boilers.

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