A MICROSTRUCTURE DEGRADATION ASSESSMENT OF 9%Cr-1.8%W FERRITIC CREEP RESISTANT STEEL EXPOSED FOR 64,363 OR 115,395 HOURS IN PLANT TRIAL APPLICATION

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ABSTRUCT

We conducted a trial application of the super heater tube and main steam pipe of the actual power plants to confirm the stability of the mechanical properties of W containing 9% Cr steel. In order to evaluate the creep resistance of the advanced steel for long-term service, we carried out precise investigations. The extension creep test resulted in good agreement of rupture strength with the lengthy creep reference curve of parent materials. Only a scarce deterioration in tensile strength was observed. Brittle-ductile transition temperature on Charpy impact test maintained longer exposure time than 13,763 hours at 569 ℃. Microstructure degradation was assessed through the martensitic lath width monitoring with the reference curve and measurement of the grain boundary shield ratio by $M_{23}C_6$ type carbide or Fe_2W type Laves phase. Both methods evaluate the martensitic dislocation sub-structure stability for high temperature creep through Transmission Electron Microscopy (TEM). The grain boundary shield ratio measurement method indicated that the new assessment methodorogy is accurate. As for the precipitation strengthening of the lath interior, the coarsening of (Nb,V)(C,N) type precipitation was monitored by the V-Wing type MX precipitates length measurement. The length of stable V-Wing type MX monitoring is possibly a functional index for the microstructural development if the reference curve is defined based on a large number of experiments. W precipitation amount quantification in extracted residue analyses of ex-serviced products is useful for the exposure time assessment at the application temperature.

1 Introduction

9%Cr-1.8%W containing ferritic heat resistant steel (ASME SA213 T92, KA-STBA29) is an advanced steel product for high temperature application in USC power plants. In order to certify the high temperature properties, long-term trial application in an actual power plant is required. Metallurgical investigation of the ex-serviced material after several ten thousand years or longer provides information on the materials degradation and makes a relative assessment of the microstructural stability. In this paper, metallurgical indexes for the microstructure development of the advanced W containing martensitic steel are suggested and discussed for specimens after ca. 65,000 hours and 115,000 hours trial use in actual USC coal-fired boilers.

2 SERVICE CONDITIONS AND METALLURGICAL INVESTIGATION METHODS

2.1 Chemical compositions and dimensions of the products in service

Table 1 indicates the chemical compositions of the products, super heater tube and main steam pipe. The dimensions of the tube are 38.1 mm in outer diameter and 6.0 mm in wall thickness. Those for the pipe are 352mm in O.D. and 56mm in wall thickness. The ingot of the products was melted in an electric furnace and refined by vacuum ladle. The billet was forged to the pipe or hot extruded to the tube. The products were normalized at 1070 or at 1100℃ for 60 or 12 minutes respectively and tempered at 780℃ for 60 minutes.

Table 1. Chemical compositions of the products for trial application in actual USC boilers

Products	C	Si	Mn	Cr	Mo	W	Nb	V	N	Al	B
Tube	0.09	0.06	0.45	9.01	0.50	1.77	0.05	0.20	0.048	0.010	0.004
Pipe	0.10	0.10	0.47	9.05	0.49	1.72	0.06	0.21	0.037	<0.005	0.002

2.2 Service conditions and evaluation interval

The super heater tube was applied at 569 °C of steam temperature and at 19.3 MPa, of steam pressure. The main steam pipe was exposed at 560 °C of steam temperature and at 25.4 MPa of steam pressure. In order to monitor the microstructural stability, tubes were taken partially in a sequential order of operation times at 13,763 hours, 21,272 hours, 44,456 hours, and 115,395 hours. The main steam pipe was ex-serviced after 64,363 hours exposure.

2.3 Tensile, creep and toughness properties

To evaluate the toughness stability of the specimens, 2mm depth V-notch Charpy impact test specimens with 5×10 mm square column in cross section and 55 mm in length were taken. Tensile test specimens and creep specimens were taken from the tubes with 6 mm in thickness parallel to the L-direction. The gage lengths were 30 mm for both specimens.

2.4 Microstructure degradation indexes

Four kinds of metallurgical indexes were used to assess the microstructure degradation of the ex-serviced materials. The thin foil and replica specimens with different operating durations of application components were compared for the microstructural degradation monitoring through the TEM observation.

2.4.1. W precipitation as an index of exposure duration at the service conditions

W precipitation amount measurement implies the attainment of the equilibrium condition of W solution at service temperature from the hyper solution at the beginning of the service. X-ray diffraction qualification and photochemistry quantification of the extracted residue were used to analyze the W precipitation amount and the composition.

2.4.2. Precipitation strengthening effect monitoring at lath interior

Precipitation morphology monitoring especially on the V-Wing (Hamada [1]) type MX is also suggested in this work as the reference index of the microstructural degradation. The ideal shape of the V-Wing precipitate with the coupled corns that contact with each other at the bottom possibly represents MX type carbo-nitride coarsening. With the V-Wing length increase, MX type carbo-nitride coarsens. The new index for precipitation coarsening at the lath interior emphasizes the accuracy of fine MX particle size measurement.

2.4.3 Stability of the martensitic sub-grain microstructure

W precipitation possibly affects the microstructural degradation through the grain boundary precipitation fixing mechanism. We suggested the creep rupture strength using the grain boundary shield ratio in the following equation (Hasegawa [2]):

$$\sigma_C = \frac{MGb}{2}\sqrt{\rho_0}\exp(-Kt^{n\frac{f_0}{f}}) \ , \ f = \left(\frac{\sum fi}{L}\right)^2 \quad \text{--} \quad (1)$$

Here, the nomenclature σ_C is the creep rupture strength, M is the Taylor's factor, G is the modulus of elasticity, ρ_0 is the dislocation density before service, t is the service duration and f is the grain boundary shield ratio by precipitates as defined in the latter equation (1). The fi is the grain boundary occupation length by precipitates and L is the grain boundary length. Each of these, boundary lengths except the lath boundary was observed through TEM on thin foil. TEM analyses prognosticate the remnant creep life in Equation (1). If the sub-grain microstructure is the member of creep resistance, the lath width growing through the dynamic recrystallization might be an important index for martensitic steels. The lath width was observed in photos to decide the mean values for each specimen, and microstructural damage was evaluated through comparison with the reference curve (Sawada [3]).

3 EXPERIMENTAL RESULTS

3.1 Creep resistance of the ex-serviced products

Figure 1 shows the extension creep rupture test results of ex-serviced tubes. Each character distinguishes monitoring time. "×" is that for the parent material, before service. The other characters were estimated rupture time by using of the Larson-Miller Parameter from steam temperature at 569 °C to the extension creep temperature at 600 °C in order to compare the plots with the averaged rupture curve of ASME standard at 600 °C. The extension creep test of lengthy serviced products indicated good agreement with that of the averaged ASME rupture curve.

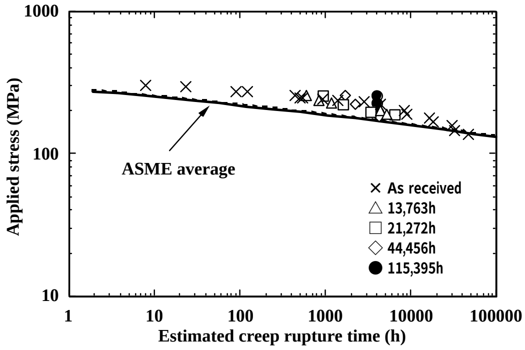

Figure 1. Creep resistance evaluation by extension creep for the ex-serviced tubes compared with that of the parent material at 600°C.

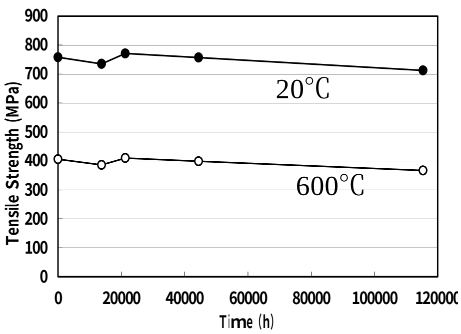

Figure 2. Stable tensile strength with exposure times for the tubes

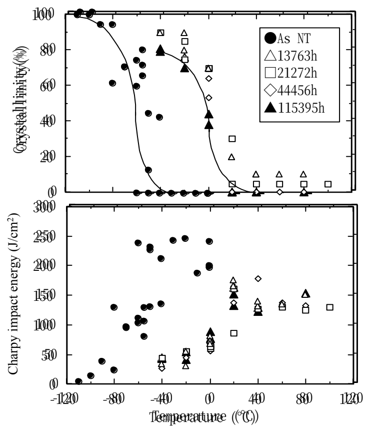

Figure 3. Charpy transition curves alteration with exposure times for the tubes.

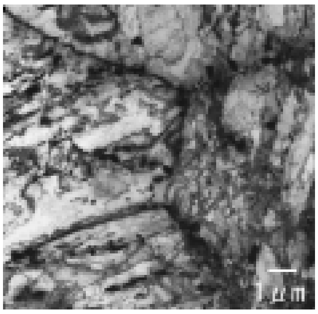

Figure 4-1. TEM image of thin foil for the tube after 44,456 hours in service at steam temperature of 569°C.

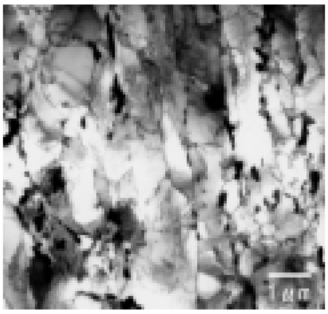

Figure 4-2. TEM image of the pipe after 64,363 hours exposure at steam temperature of 560 °C. A slight lath structure recovery is apparent.

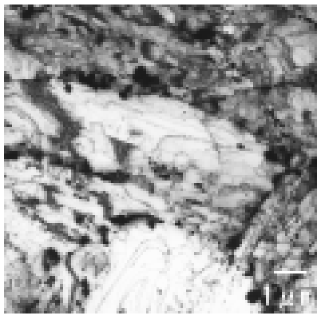

Figure 4-3. A sub-grain microstructure developed after 115,35 hours exposure at steam temperature of 569 °C.

3.2 Tensile properties and toughness degradation

Figure 2 shows the tensile and toughness properties for ex-serviced tubes. Tensile strength hardly decreased from those of the parent material over time. Charpy transition temperatures of the tubes were also stable after 13,763 hours exposure. The shelf energies of the aged tubes stayed at about 150 J/cm^2. The values of absorbed energy are sufficiently high for the boiler components even at 0 °C as indicated in Figure 3. Consequently, the tensile and toughness properties are sufficient for actual application.

3.3 Sub-grain microstructure degradation

Figures 4-1 to 4-3 show the sub-grain microstructures of the thin foils for the 44,456, 64,363 and 115,395 hours exposed products through TEM. These steels have the tempered martensitic microstructures for all exposure times before complete microstructural recovery. Figures 4 show the distinct tempered martensitic lath structure for all exposure times. The sub-grain microstructure does not appear to have been severely damaged. The lath width was measured in the photos as indicated in these figures. By comparing the three photos, it is possible to see the relative degradation over time of the lath structures.

4 DISCUSSIONS: METALLURGICAL DEGRADATION ASSESSMENT OF GR.92

4.1. Creep exposure time reference curve for W precipitating steel

Figure 5 shows the increase of W precipitation amount increase as a function of creep exposure time. The solution limit of W at 560°C for the installed materials is about 0.3 mass% according to the calculated equilibrium condition by Thermo-calc. . The remnant 1.45 mass% W precipitates mainly as inter-metallic compound, Fe_2W type Laves phase, during the creep. The driving force of W precipitation derives from the excess W amount in the matrix. Therefore, the W precipitation amount is decided by the exposure time, temperature and the excess W content. Uniform precipitation phenomenon is fitted by Kormogolov -Johnson-Mehl-Avrami type equation (Avrami [4]):

$$w(t)=1-\exp\{-(kt)^n\} \qquad \text{--} \qquad (2)$$

Here, k and n are the phenomenological constants and w(t) is the precipitation fraction as a function of t. Laves phase segregates at grain boundaries. Therefore, k and n are no more than fitting parameters. However the precipitation curve with Equation (1) in Figure 5 is a useful reference curve for the exposure time index. The index possibly compensates for the uncertainty of metal temperature for the super heater tube and the daily or weekly plant operation temperature variation. The reference curve indicates the corresponding exposure time at service temperature. In Figure 5, n and k values in Equation (2) are 0.2856 and 2.593×10^{-4}

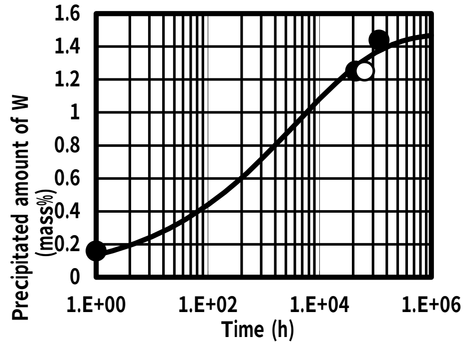

Figure 5. W precipitation during creep
●: lengthy serviced tubes, ○: ex-serviced pipe respectively.

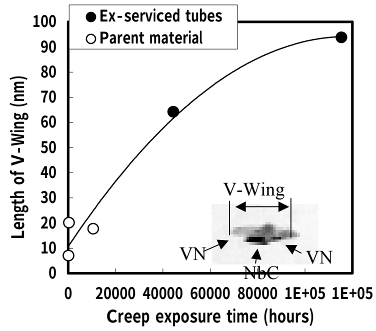

Figure 6. Monitoring of the length of V-Wing type MX for the tubes (●) and parent materials (○)

4.2. Precipitation coarsening index, V-Wing length monitoring

MX type carbo-nitride, (Nb,V)(C,N), is an effective obstacle against the dislocation glide on a slip plane. Most of Nb and V precipitates during heat treatment. However the remnant V may precipitate as V(C,N) on the (Nb,V)(C,N) precursor. Ostwald ripening occurs also during lengthy creep. The length of V-Wing is a candidate index for the MX precipitation coarsening. Figure 6 shows the V-Wing length increase over exposure time. The wing part of V-Wing consists of VN, and its growth rate is determined by the diffusion of V and nucleation process. This mechanism explains the length increase tendency of Figure 6. The radius increase of the equivalent sphere of the precipitates was reported for the Gr.92 steel (Hald [5]). However the equivalent radius measurement of (Nb,V)(C,N) eliminating the other precipitates is inadequate for monitoring of MX ripening unless the element qualification instrument is equipped with an electron microscope having an image analyzer (Letofsky [6]). Therefore, V-Wing length measurement may be ablie to replaces the MX ripening evaluation method as a simple index if the reference curve is derived from many reliable measurements.

4.3. Microstructural degradation indexes, the lath width and the grain boundary shield ratio monitoring

Figure 7 is the measured mean lath width of 44,456 hours and 115,395 hours serviced tubes by TEM observation and that of the 64,363 hours serviced pipe for open circle character with error bar. The closed mark is the data for the other advanced martensitic steels, 9% and 11% Cr steels with W or Mo (Sawada [3]). Normalized lath width λ, calculated by using initial lath width L_0 and that in a ruptured specimen corresponds to the equilibrium value L_e as $\lambda=(L-L_0)/(L_e-L_0)$, of each specimen almost agree with the averaged line of the reference curve. Nomenclature L means the averaged lath width of the data of more than 100 measurements in the TEM photo. But the data scattering is insufficiently small to determine an accurate microstructural degradation assessment. Estimated creep strain reaches 0.025 in Figure 7 because of the wide error range. The error range is almost 20 % if the lath width saturate for a larger creep strain than 0.12. Lath width measurement and its comparison with a reference line give only the rough creep life. Less than 30 % of the creep life is consumed according to Figure 7. Figure 8 shows the estimated creep rupture strengths of the ex-serviced materials for each exposure time converted to those at 600 ℃ by LMP. The creep rupture strengths calculated by Equation (1) were in good agreement with the averaged rupture strength of the ASME standard. An initial constant $f_{0,}$ experimentally measured to 0.025 by TEM, is based on the $M_{23}C_6$ type carbide precipitation shield ratio before service. K and n for fitting parameters are 0.3603 and 0.19 at 600 ℃.

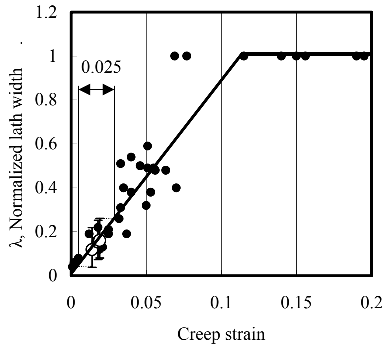

Figure 7. Comparison of the normalized lath width of ex-serviced products (○) and the other martensitic advanced creep resistant steels (●) with reference line.

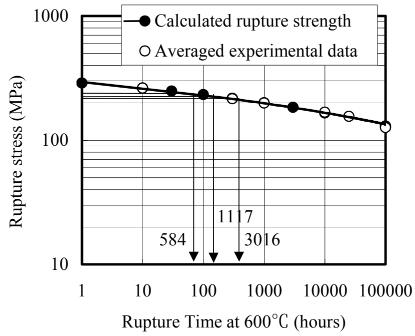

Figure 8. Agreement of the estimated creep rupture strength by Equation (1) with the experimental data
Rupture strength estimates the equivalent exposure time accurately.

Precipitation shield ratios were 0.558 and 0.488 for tubes after 44,456 hours and 115,395 hours exposure, and 0.516 for pipe after 64,363 hours exposure by TEM photo analyses. The equivalent exposure time of pipe at 600 ℃ are 584 hours, and those for tubes at 600 ℃ are 1,117 and 3,016 hours according to Figure 8. Applied stresses for the trial plant test were smaller than 100 MPa. Therefore, the rupture strength deterioration corresponding to the microstructural degradation appears small in Figure 8. This tendency explains the small deterioration of the tensile strength of ex-serviced products. A good agreement of the calculated rupture strength by using Equation (1) indicates the most accurate and certain prognostication methodology in measurement of a grain boundary shield ratio by precipitates.

4 CONCLUSIONS

1. Only a small degradation was observed in mechanical properties, tensile strength, Charpy transition temperatures change and extension creep resistance after several 10 to 100 thousand hours trial use in an actual plant as super heater tubes and main steam pipe.
2. Based on the dislocation sub-structure creep rate determining process, the grain boundary shield ratio measurement and the rupture strength estimation method using Equation (1) was the most functional microstructure degradation index for the obtained experimental results.
3. Direct microstructural evolution assessment, lath width evaluation was not as effective for the remnant creep life prediction because of the large data scattering for the specimens that were relatively undamaged.
4. From the viewpoint of the precipitation strengthening mechanism, the V-Wing type (Nb,V)(C,N) length was measured as a microstructural degradation index. A certain reference curve derived from a large number of measurements might suggest a new assessment method for V-Wing precipitating steels.
5. W precipitation amount measurement is useful only for the exposure time assessment for the application temperature. W precipitation was driven by the excess solved W amount and not related to the degradation.

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