Effect of Initial Microstructure on Creep Strength of ASME Grade T91 Steel

Kota SAWADA,^{1)*} Kaoru SEKIDO,¹⁾ Kazuhiro KIMURA,¹⁾ Ko ARISUE,²⁾ Masaki HONDA,²⁾ Nobuyoshi KOMAI,²⁾ Norihide FUKUZAWA,³⁾ Tomonori UENO,³⁾ Nobuaki SHIMOHATA,⁴⁾ Hitoshi NAKATOMI,⁴⁾ Kenji TAKAGI,⁴⁾ Takahiro KIMURA,⁵⁾ Kyohei NOMURA⁵⁾ and Keiji KUBUSHIRO⁵⁾

1) National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki, 305-0047 Japan.

2) Mitsubishi Heavy Industries, Ltd., 5-717-1, Fukahori-Machi, Nagasaki, 851-0392 Japan.

3) Hitachi Metals Ltd., 1240-2, Hashima-cho, Yasugi, Shimane, 692-8601 Japan.

4) Electric Power Development Co., Ltd., 15-1, Ginza 6-Chome, Chuo-ku, Tokyo, 104-8165 Japan.

5) IHI Corporation, 1, Shin-nakahara-cho, Isogo-ku, Yokohama, 235-8501 Japan.

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To clarify the cause of heat-to-heat variation in the creep strength of Grade T91 steels, the influence of the initial microstructure on creep strength was investigated. The distribution of chromium concentration considered to be remaining segregation was observed as corresponding to lamellar contrasts parallel to the longitudinal direction of the boiler tube. Standard deviation (SD) of ΔCr was employed as an indicator of the degree of segregation, and a good correlation was found between the SD of ΔCr and the creep rupture life at 650°C. Remaining segregation was reduced by renormalizing heat treatment at 1 200°C instead of 1 250°C. The creep rupture life of steel subjected to renormalizing heat treatment at 1 200°C and tempering at 760°C, followed by normalizing and tempering under standard heat treatment conditions for Grade T91 steel, was prolonged by a factor of 2.3–2.8. The strengthening effect of renormalizing at 1 200°C to reduce the remaining segregation was confirmed by creep tests up to about 10 000 h at 600°C and 650°C. Decreases in the number density of M_{23}C_6 carbide particles, length of high-angle boundaries and average KAM values during creep exposure are promoted by the presence of remaining segregation. Since diffusion is enhanced by the concentration gradient of elements, degradation due to microstructural change is promoted by the presence of remaining segregation. Segregation should be reduced to obtain high creep strength with homogenized concentration of chemical composition.

KEY WORDS: creep strength enhanced ferritic steel; T91; creep strength; segregation.

1. Introduction

Many types of creep strength enhanced ferritic (CSEF) steels have been developed for boiler tubes, main steam pipes and headers in thermal power plants after modified 9Cr-1Mo steel was standardized as Grade 91 in the early 1980s.¹⁾ CSEF steels improve the steam temperature and thermal efficiency of thermal power plants due to their higher strength at elevated temperatures compared to that of conventional steels. However, it has been pointed out that the creep strength of CSEF steel degraded in the long-term.^{2–4)} Creep strength of CSEF steels was found to be lower in welded joints than in the base metal.⁵⁾ Therefore, the material specifications and allowable stress have been reviewed based on the re-evaluation of the creep strength of CSEF steels.^{6–8)} Moreover, the weld strength reduction factors and creep life evaluation equation have also been determined for CSEF steels.^{9–12)}

In Japan, the allowable stress for modified 9Cr-1Mo steel

was revised in 2007 and 2014 based on the re-evaluation of creep strength.^{7,8)} However, the Assessment Committee on Creep Data of High Chromium Steels proposed a further revision in 2015 because the new creep strength data obtained after the 2014 review showed relatively low creep strength.¹³⁾ It has been reported for boiler tubes used in the NIMS Creep Data Sheet Project that the creep strength of the tubes sampled in 2000 and 2001 was lower than that of the tubes sampled in 1990.¹⁴⁾ Therefore, to clarify the reason for the heat-to-heat variation in the creep strength of ASME SA-213/SA-213M Grade T91 steels, the effect of the initial microstructure on creep strength was investigated.

2. Experimental Procedures

The materials examined were modified 9Cr-1Mo steel tubes for boilers (ASME SA-213/SA-213M Grade T91). Six heats obtained from the NIMS Creep Data Sheet were selected for investigation. Chemical compositions, heat treatment conditions, product dimensions and austenite grain size number are listed in **Table 1** together with the requirements for chemical composition and heat treatment condi-

* Corresponding author: E-mail: SAWADA.Kota@nims.go.jp
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Table 1. Chemical composition (mass%), heat treatment condition, size of tube and grain size number of the steels studied.

		C	Si	Mn	P	S	Ni	Cr	Mo	V	Nb	N	Al	Ti	Zr
Spec.	METI	0.07	0.20	0.30	≤0.020	≤0.010	≤0.40	8.0	0.85	0.18	0.06	0.030	≤0.04	–	–
	ASME	–0.14	–0.50	–0.60				–9.5	–1.05	–0.25	–0.10	–0.070	≤0.02	≤0.01	≤0.01
	MGA	0.10	0.38	0.40	0.015	0.001	0.12	8.53	0.96	0.21	0.076	0.050	0.014	<0.001	<0.001
	MGB	0.09	0.34	0.45	0.015	0.001	0.20	8.51	0.90	0.205	0.076	0.042	0.016	0.001	<0.001
	MGC	0.09	0.29	0.35	0.009	0.002	0.28	8.70	0.90	0.22	0.072	0.044	0.001	<0.001	<0.001
	MGD	0.10	0.29	0.41	0.010	0.001	0.10	8.41	0.90	0.185	0.07	0.048	0.016	0.001	<0.001
	MGF	0.11	0.25	0.42	0.013	0.001	0.06	8.41	0.91	0.20	0.08	0.053	0.001	0.006	<0.001
	MGG	0.10	0.38	0.37	0.018	0.002	0.12	8.60	0.95	0.190	0.08	0.0458	0.002	<0.001	<0.001
		Normalizing				Tempering			Dimension		G.S.				
Spec.	METI	≥1 040°C				≥730°C			–		–				
	ASME	1 040–1 080°C				730–800°C			–		–				
	MGA	1 045°C/10 min. AC				780°C/60 min. AC			50.8 OD, 8.0 t		10.1				
	MGB	1 050°C/60 min. AC				760°C/60 min. AC			50.8 OD, 7.3 t		9.3				
	MGC	1 050°C/10 min. AC				765°C/30 min. AC			50.8 OD, 8.0 t		10.2				
	MGD	1 050°C/10 min. AC				780°C/40 min. AC			50.8 OD, 8.9 t		10.2				
	MGF	1 045°C/60 min. AC				780°C/60 min. AC			50.8 OD, 8.7 t		10.6				
	MGG	1 050°C/15 min. AC				790°C/60 min. AC			50.8 OD, 9.0 t		10.7				

METI: The Interpretation for the Technical Standard for Thermal Power Plant, KA-STBA28

ASME: Boiler and Pressure Vessel Code, SA-213/SA-213M Grade T91

AC: air cooling

OD: outer diameter

t: thickness

tions in the ASME specifications¹⁵⁾ and KA-STBA28.¹⁶⁾ The chemical compositions and heat treatment conditions of all investigated steels are within the range of these specifications. Creep tests were performed under constant load in air, using specimens 30 mm in gauge length and 6 mm in gauge diameter. Microstructures of as-received samples, gauge and grip portions of creep ruptured samples, were observed by optical microscopy, SEM and TEM, and analyzed using EPMA, SEM-EDS and SEM-EBSD. Vilella's Solution was used for etching for optical microscopy.

3. Results and Discussion

3.1. Creep Strength Properties

Stress versus time-to-rupture curves for the six heats at 600°C, 625°C and 650°C are shown in **Fig. 1**. The creep strengths of MGD, MGF and MGG were lower than those of MGA, MGB and MGC. The difference in creep strength increased with increasing testing temperature. It was reported that Ni and Al decrease the creep strength.^{5,17)} However, at 650°C, no correlation was observed between the heat-to-heat variation of the creep strength for the six heats and the amount of Ni and Al. No effect of the Al content on creep strength has been reported¹⁸⁾ when the Al content was less than 0.025 mass%. In short, no correlation was observed between the creep strength and Al content because the Al content of the six heats was less than 0.025 mass%.

3.2. Microstructural Observation

For the as-received MGA heat sample, an optical micro-

Fig. 1. Creep rupture strengths of MGA, MGB, MGC, MGD, MGF and MGG heats of Grade T91 steel at 600, 625 and 650°C.

graph of a cross section parallel to the longitudinal direction is shown in **Fig. 2**. A large number of layered contrasts were observed parallel to the longitudinal direction of the boiler tube. Layered contrasts were also confirmed for other heats.

For the as-received MGD heat sample, elemental maps of Cr, C, V and Nb obtained by EPMA are shown in **Fig. 3**. Layers with a high concentration of alloying elements were observed parallel to the longitudinal direction of the boiler tube. The concentration of Cr, C, V and Nb was high

Fig. 2. Macrostructure of MGA heat of Grade T91 steel in the as received condition.

Fig. 3. Elemental maps of EPMA on chromium, carbon, vanadium and niobium of MGD heat of Grade T91 steel in the as received condition. (Online version in color.)

in the same area.

Also for the as-received MGD heat sample, elemental maps of Cr, Nb, V and Al on carbon-extracted replica were obtained by STEM-EDS, as shown in Fig. 4. $M_{23}C_6$ carbides shown in red and V-rich MX particles shown in blue were distributed throughout the area. A large number of Nb-rich MX particles shown in green and inclusions (Al_2O_3) shown in white were aligned along the longitudinal direction, together with $M_{23}C_6$ carbides and V-rich MX particles.

Consequently, the layered contrasts shown in Fig. 2 correspond to layers with a high concentration of alloying elements and a large number of precipitates and inclusions. It is presumed that the areas where alloying elements concentrated due to solidifying segregation were thinly rolled by hot extrusion, causing the formation of a layered microstructure with a different concentration of alloying elements.

In order to compare the area containing solidifying segregation (segregation zone) and other areas, the IPF map for the as-received MGA heat sample was observed by SEM-EBSD, as shown in Fig. 5. The black triangle at the top center of the figure is an indentation indicating the location of the segregation zone. The sizes of prior austenite grains, packets and blocks were smaller in the segregation zone (B) than in the other area (A). In the segregation zone, the growth of prior austenite grains may be retarded by the presence of undissolved Nb-rich MX particles that remained even after normalizing at 1 050°C.

Hardness (HV 0.05) distribution along the thickness

Fig. 4. STEM-EDS image of carbon extracted replica taken from MGD heat of Grade T91 steel in the as received condition. (Online version in color.)

Fig. 5. IPF map of MGA heat of Grade T91 steel in the as received condition. (Online version in color.)

direction for the as-received samples of six heats is shown in Fig. 6. The distribution of hardness was constant for MGA, MGB and MGC. On the other hand, for MGD and MGG, the hardness was slightly higher at the outer surface than at the inner surface of the tube. In the case of MGF, the hardness was lower at the outer surface than at the inner surface. Therefore, the distribution of the microstructure along the thickness direction is homogeneous for MGA, MGB and MGC, as compared with the other heats.

3.3. Segregation of Alloying Elements

In Section 3.2, it was confirmed that the segregation zone was distributed in layers along the thickness direction. The relationship between the segregation zone and the creep strength is discussed in this section based on the quantitative evaluation of the segregation zone.

Many Nb-rich MX particles remain undissolved after normalizing at 1 050°C, although most $M_{23}C_6$ carbides are dissolved during normalizing.^{19–21)} As-received samples were renormalized for 10 min at 1 050°C. SEM image for MGG after renormalizing is shown in Fig. 7. Band-like regions that are not deeply etched compared with other areas were observed along the longitudinal direction of the tube. These

Fig. 6. Distribution of micro Vickers hardness through wall thickness of Grade T91 steels.

Fig. 7. Secondary electron image of MGG heat of Grade T91 steel after renormalizing for 10 min. at 1 050°C.

band-like regions may have high corrosion resistance since the Cr concentration is high due to the dissolution of a large number of $M_{23}C_6$ carbides.

Cr maps for MGA, MGB and MGG after renormalizing for 10 min at 1 050°C were obtained from SEM-EDS, as shown in Fig. 8. The mapping location was around the center of the wall thickness. Many band-like regions with high Cr content were observed in MGG. The same tendency was confirmed in MGA. However, the change in contrast corresponding to the Cr content distribution was small in MGB. The Cr content changes along the wall thickness direction although the change along the longitudinal direction of the tube is small. The elemental map in Fig. 8 consists of 200 (longitudinal direction) $\times$ 256 (wall thickness direction) pixels. The average Cr content for 200 pixels along the longitudinal direction of the tube is plotted against the distance in the wall thickness direction for MGA, MGB and MGG, as shown in Fig. 9. The fluctuation width of

Fig. 8. Chromium mapping of MGA, MGB and MGG heats of Grade T91 steel renormalized for 10 min. at 1 050°C. (Online version in color.)

Fig. 9. Distribution of average chromium concentration along wall thickness of MGA, MGB and MGG heats of Grade T91 steel.

Fig. 10. Schematic illustration on the definition of ΔCr .

the average Cr content for MGG was largest among the steels; for example, it was three times larger in MGG than in MGB. The fluctuation width of MGA was between those of MGB and MGG. The standard deviation of the average Cr content in the range of 1 mm along the wall thickness direction was estimated for all six heats. No correlation was observed between the standard deviation and the creep strength. Fick's first law of diffusion is expressed as

$$J = -D(dC/dx) \dots\dots\dots (1)$$

where J is the flux, D is the diffusion coefficient, C is the concentration and x is the distance. dC/dx corresponds to the concentration gradient. The diffusion is promoted in proportion to the increase in concentration gradient. Therefore, a measure for quantitatively expressing the concentration gradient was proposed using the distribution of the average Cr content shown in Fig. 9.

Figure 10 shows a schematic drawing of the proposed measure. The difference between the maximum and minimum Cr content, ΔCr , at a constant distance (x) was

Table 2. Standard deviation of ΔCr along wall thickness.

Heat	MGA	MGB	MGC	MGD	MGF	MGG
SD	0.060	0.047	0.063	0.068	0.068	0.079

estimated in the range of 1 mm along the wall thickness direction. The standard deviation of ΔCr along the wall thickness direction is defined as the measure for expressing the concentration gradient of Cr. The width and number of segregation zone changes along the wall thickness direction and depends on the heat, as shown in Fig. 8. It was assumed that the standard deviation of ΔCr along the wall thickness direction was regarded as the measure for expressing the difference in the width and number of segregation zones among the steels. The standard deviation of ΔCr was estimated when the value of x was changed from 8 to 100 μm . A strong relationship between the standard deviation and creep strength was confirmed when the value of x was about 40 μm . The standard deviation of ΔCr estimated when the x value is 40 μm is listed for each of the six heat samples in Table 2. The value of ΔCr in the range of 40 μm successfully corresponds to the concentration gradients because the width of the segregation zone is about 10–20 μm for the steels studied.

Figure 11 shows the relationship between the standard deviation of ΔCr and the time to rupture at 650°C under 50, 60, 70 and 80 MPa for the six heat samples. The time to rupture decreased with increasing the standard deviation under all the stress conditions. The correlation between the standard deviation and time to rupture becomes strong under low-stress conditions in the long term. Consequently, the creep rupture strength tends to decrease when the distribution of Cr concentration is drastic due to the solidifying

segregation.

It is predicted that other alloying elements besides Cr are also segregated. The contents of the other alloying elements are less than 1 mass% although the Cr content of the steels studied is more than 8 mass%. Therefore, we focused on the Cr content with a large content fluctuation.

3.4. Effect of Reduction of Segregation on Creep Strength

In Section 3.3, the correlation between the standard deviation of ΔCr in the width range of 40 μm and the time to rupture was confirmed. The time to rupture decreased when the Cr segregation was strong, as shown in Fig. 11. We tried to reduce the segregation by heat treatment and investigated the effect of the reduction on the creep strength.

The Cr maps obtained by SEM-EDS for MGG renormalized for 10 min at 1 050°C, 10 min at 1 200°C and 20 h at 1 200°C are shown in Fig. 12. The Cr distribution after renormalization at 1 200°C was homogeneous although a large number of Cr segregation zones were observed after renormalization at 1 050°C. Homogeneous Cr distribution may be achieved since atomic diffusion can be promoted at 1 200°C as compared with 1 050°C. Furthermore, the

Fig. 11. Relation between time to rupture at 650°C with standard deviation of ΔCr along wall thickness.

drastic decrease in number of coarse MX particles due to the dissolution of Nb-rich MX particles can contribute to homogeneous Cr distribution at 1 200°C.^{16,17,19)}

Heat treatment was performed to reduce the segregation in MGG and MGB, as listed in Table 3. The MGG was renormalized for 60 min at 1 200°C (No. 1) and 1 250°C (No. 2). Renormalization for 60 min at 1 200°C was performed for MGB (No. 4). Prior austenite grains were extremely coarse after renormalizing at 1 200°C¹⁹⁾ although heat treatment at 1 200°C can reduce the segregation. There-

Fig. 12. Chromium mapping of MGG heat of Grade T91 steel after renormalized for (a) 10 min. at 1 050°C and (b) 10 min. at 1 200°C, and (c) 20 h at 1 200°C. (Online version in color.)

Table 3. Heat treatment condition, grain size number and hardness in the as received condition and after heat treatment.

No.	Heat	Heat treatment condition				As received		After heat treatment	
		Normalizing	Tempering	Normalizing	Tempering	G.S. No.	Hardness HV	G.S. No.	Hardness HV
1	MGG	1 200°C/60 min., AC	760°C/60 min., AC	1 050°C/30 min., AC	780°C/60 min., AC	10.7	223	9.4	231
2		1 250°C/60 min., AC						9.0	223
3		—						10.6	224
4	MGB	1 200°C/60 min., AC	760°C/60 min., AC			9.3	231	9.0	216

fore, tempering for 60 min at 760°C was performed after renormalizing at 1 200°C and 1 250°C, followed by normal normalizing for 30 min at 1 050°C and tempering for 60 min at 780°C. Heat treatment No. 3 can clarify the effect of normal normalizing and tempering on the creep strength. The prior austenite grain size is smaller in MGG than in MGB in the as-received condition. No change in prior austenite grain size was observed after the normal normalizing and tempering for MGG. On the other hand, the prior austenite grain size of MGG was coarse and almost equal to that of MGB after heat treatment to reduce the segregation. Undissolved MX carbonitrides in the segregation zone retarded the grain growth at 1 050°C. Most of these undissolved MX carbonitrides may have disappeared due to the dissolution of Nb-rich MX at a temperature higher than 1 200°C, leading to drastic grain growth at 1 200°C. No drastic change in hardness was observed between before and after heat treatment.

In Fig. 13, the average Cr content evaluated in the same way as shown in Fig. 9 is plotted against the distance in the wall thickness direction after the heat treatment listed in Table 3. The standard deviation of ΔCr after heat treatment is estimated from Fig. 13 and listed in Table 4. The results of Fig. 13 were obtained from the center of the wall thickness. The fluctuation in Cr content was small for MGG (No. 1) and MGB (No. 4) after renormalizing at 1 200°C, which means that the segregation observed in MGG in the as-received condition was reduced. On the other hand, the effect of heat treatment at 1 250°C (No. 2) on segregation is small because the fluctuation in Cr content is still large. This

indicates that 1 250°C is very close to the temperature of the two-phase region of austenite and ferrite. No drastic effect of heat treatment at 1 050°C on segregation was observed.

Figure 14 shows the stress versus time-to-rupture curve

Table 4. Standard deviation of ΔCr along wall thickness.

Heat	MGG	No. 1	No. 2	No. 3	MGB	No. 4
SD	0.079	0.04	0.058	0.059	0.047	0.044

Fig. 14. Stress vs. time to rupture curves of MGG heat of Grade T91 steel in the as received condition and after heat treatment.

Fig. 13. Distribution of average chromium concentration along wall thickness of heat treated steels.

at 650°C for MGG renormalized at 1 200°C (No. 1) and 1 050°C (No. 3), and the as-received MGG sample. The time to rupture of the heat-treated (No. 3) sample was 1.3–1.4 times longer than that of the as-received sample. The time to rupture of the heat-treated (No. 1) samples were 2.3 and 2.8 times longer than that of the as-received sample under 100 and 80 MPa, respectively.

Creep rate versus time curves for the heat-treated (No. 1) and as-received samples are shown in **Fig. 15**. Creep tests were performed at 600°C under 120 MPa and at 650°C under 70 MPa. The creep rate was smaller in the heat-treated (No. 1) sample than in the as-received sample under both creep test conditions. The creep strength was apparently improved by the reduction of segregation because the heat-treated sample was at the beginning of tertiary creep even after the as-received sample ruptured. Creep tests under low-stress conditions are ongoing. The improvements of creep strength by reduced segregation for more than 10 000 h at 600°C and 650°C will be investigated in future.

3.5. Effect of Segregation on Creep Strength

The presence of coarse prior austenite grains after heat treatment for the reduction of segregation can affect the creep strength. It was reported that in modified 9Cr-1Mo steel, no effect of grain size on creep strength was observed for about 10 000 h although long-term creep strength for about 100 000 h depends on the grain size.²²⁾ Therefore, the

coarse grains cannot explain the creep strength improvement of about 10 000 h by the heat treatment for the reduction of segregation shown in **Fig. 15**.

The number densities of $M_{23}C_6$ carbide, V-rich MX and Nb-rich MX were measured in the segregation zone and other areas. The correlation between the number density of $M_{23}C_6$ carbide and the creep strength was confirmed, while no correlation between that of MX and strength was observed. **Figure 16** shows the relationship between the number density of $M_{23}C_6$ carbide in the segregation zone and other areas and the time to rupture at 600°C and 650°C for MGB and MGG. At the segregation zone, there was no difference in the number density before creep. After creep rupture, however, the number density was drastically lower in MGG than MGB. At the outside of the segregation zone, the number densities of both the as-received and creep ruptured samples were smaller in MGG than MGB. It is concluded that the number density of $M_{23}C_6$ carbide became smaller due to the low content of alloying elements at the outside of the segregation zone compared to the inside of the segregation zone. This indicates that precipitation strengthening outside the segregation zone is smaller than that inside the segregation zone.

Figure 17 shows the relationship between the length of high-angle boundaries and the time to rupture at 600°C under 80 MPa and at 650°C under 60 MPa. The length of

Fig. 15. Creep rate vs. time curves at (a) 600°C-120 MPa and (b) 650°C-70 MPa of MGG heat of Grade T91 steel in the as received condition and after normalizing heat treatment at 1 200°C.

Fig. 16. Changes in number density of $M_{23}C_6$ carbide particles inside and outside of segregation band of MGB and MGG heats of Grade T91 steel during creep exposure at (a) 600°C and (b) 650°C.

Fig. 17. Changes in length of high angle boundaries for inside and outside of segregation band of MGB and MGG heats of Grade T91 steel during creep exposure at 600°C-80 MPa and 650°C-60 MPa.

Fig. 18. Changes in average KAM value for inside and outside of segregation band of MGB and MGG heats of Grade T91 steel during creep exposure at 600°C-80 MPa and 650°C-60 MPa.

the high-angle boundaries was measured in the segregation zone and other areas. In this case, a high-angle boundary means a boundary with a misorientation angle of 5° to 180° . The length of high-angle boundaries before creep was larger in MGG than in MGB for the segregation zone and other areas. This corresponds to the fine grains of MGG as compared with MGB. However, the length of the high-angle boundary of MGG significantly decreased after creep exposure as compared with MGB. This decrease was larger at 650°C than at 600°C.

The relationship between the kernel average misorientation (KAM) and the time to rupture is shown at 600°C under 80 MPa and at 650°C under 60 MPa in **Fig. 18**. The KAM was measured in the segregation zone and other areas. The KAM value is the average of the entire measurement area. The KAM decreased after creep rupture in MGB and MGG. The KAM of MGG significantly decreased at 650°C as compared with MGB although the decrease in MGB was almost the same as that in MGG at 600°C. The decrease in dislocation density after creep may be faster in MGG than in MGB because the correlation between the KAM and dislocation density has been confirmed.²³⁾

Consequently, the decrease in number density of $M_{23}C_6$, length of high-angle boundary and dislocation density was significant in both the segregation and non-segregation zones of MGG with strong segregation, leading to the

acceleration of the recovery of martensite. In strongly segregated steel, prior austenite grains are very fine due to the pinning effect of undissolved precipitates. Furthermore, the concentration gradient of alloying elements can promote microstructural changes due to diffusion in the segregated steel. The concentration gradient of Fe was also confirmed in the same way as Cr shown in Fig. 9. The concentration gradient of Fe can promote the recovery of martensite due to the diffusion of Fe. The concentration gradient of Cr can accelerate the coarsening of $M_{23}C_6$ due to Cr diffusion, indicating that the decrease in the number density of $M_{23}C_6$ pinned to a high-angle boundary can be promoted. Creep strength degradation in segregated steel can mainly be attributed to microstructural changes by diffusion because the heat-to-heat variation in creep strength is significant at higher temperatures. To obtain good creep properties, it is necessary to reduce the segregation since microstructural changes due to diffusion are promoted by the concentration gradient of the alloying elements.

4. Conclusions

To clarify the reason for the heat-to-heat variation in the creep strength of ASME SA-213/SA-213M Grade T91 steels, the effect of the initial microstructure on the creep strength was investigated. The results are summarized as

follows.

(1) Heat-to-heat variation in creep strength was observed in the six steels examined. The variation increased with increasing testing temperature. No correlation was found between the creep strength and Ni and Al contents at 650°C showing apparent heat-to-heat variation in creep strength.

(2) A large number of layered contrasts were observed parallel to the longitudinal direction of the boiler tube. Many precipitates and inclusions were observed in the layered contrasts region. It was predicted that the areas where alloying elements concentrated due to solidifying segregation were thinly rolled by hot extrusion, causing the formation of a layered microstructure with a different concentration of alloying elements.

(3) The difference between the maximum and minimum Cr content, ΔCr , at a constant distance (x) was defined based on the Cr content distribution along the wall thickness direction. A good correlation was found between the standard deviation of ΔCr and the time to rupture when the x value was about 40 μm .

(4) The segregation was reduced after renormalizing at 1 200°C. No clear reduction of segregation was observed after renormalizing at 1 250°C. This can be attributed to the fact that 1 250°C is very close to the temperature of the two-phase region of austenite and ferrite.

(5) Renormalizing at 1 200°C and tempering at 760°C followed by normal heat treatment of normalizing for 30 min at 1 050°C and tempering for 60 min at 780°C extended the creep rupture life by a factor of about 2.3–2.8 at 650°C under 80 and 100 MPa. The improvement in creep strength by the reduction of segregation was also confirmed under long-term conditions such as 650°C/6 920 h and 600°C/11 122 h.

(6) The decrease in number density of $M_{23}C_6$, length of high-angle boundaries and dislocation density was significant in both the segregation and non-segregation zones for strongly segregated steel. This indicates that the recovery of martensite was promoted by the large concentration gradient of alloying elements in strongly segregated steel.

(7) Consequently, the presence of segregation decreases the creep strength since microstructural changes controlled by diffusion are promoted due to the segregation. It is necessary to reduce the segregation and obtain a homogeneous distribution of alloying elements to improve the creep strength.

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REFERENCES

- 1) F. Masuyama: *ISIJ Int.*, **41** (2001), 612.
- 2) V. Foldyna, Z. Kuboň, A. Jakobová and V. Vodárek: Microstructural Development and Stability in High Chromium Ferritic Power Plant Steels, The Institute of Materials, London, (1997), 73.
- 3) A. Strang and V. Vodarek: Microstructural Stability of Creep Resistant Alloys for High Temperature Plant Applications, The Institute of Materials, London, (1998), 117.
- 4) H. Kushima, K. Kimura and F. Abe: *Tetsu-to-Hagané*, **85** (1999), 841 (in Japanese).
- 5) S. J. Brett, D. L. Oates and C. Johnston: Proc. Creep & Fracture in High Temperature Components – Design & Life Assessment Issues, DEStech Publications, Inc., Lancaster, (2005), 563.
- 6) ASME BPV Code Case 2864: 2016, 9Cr-1Mo-V Material Section I.
- 7) Thermal and Nuclear Power Engineering Society: The Material Specification in the Technical Regulation of Equipment for Thermal Power Plant, TENPES, Tokyo, (2007), 153 (in Japanese).
- 8) Thermal and Nuclear Power Engineering Society: The Material Specification in the Technical Regulation of Equipment for Thermal Power Plant, TENPES, Tokyo, (2014), 147 (in Japanese).
- 9) M. Tabuchi and Y. Takahashi: Proc. ASME 2006 Pressure Vessels and Piping/ICPVT-11 Conf., ASME, New York, (2006), PVP2006-ICPVT-11-93350.
- 10) M. Yaguchi, T. Matsumura and K. Hoshino: Proc. ASME 2012 Pressure Vessels and Piping Conf. (PVP2012), ASME, New York, (2012), PVP2012-78393.
- 11) The Life Evaluation Formula of High Chromium Steels for Thermal Power Plant, Nuclear and Industrial Safety Agency (NISA), The Ministry of Economy, Trade and Industry (METI), NISA-234c-05-9, (2005), http://www.meti.go.jp/policy/safety_security/industrial_safety/oshirase/2005/files/171214-1.pdf, (accessed 2005-12-14) (in Japanese).
- 12) The Life Evaluation Formula of High Chromium Steels for Thermal Power Plant, The Ministry of Economy, Trade and Industry (METI), (2014), http://www.meti.go.jp/policy/safety_security/industrial_safety/oshirase/2014/06/2606303-.html, (accessed 2014-5-30) (in Japanese).
- 13) K. Kimura and M. Yaguchi: Proc. ASME 2016 Pressure Vessels and Piping Conf. (PVP2016), ASME, New York, (2016), PVP2016-63355.
- 14) NIMS Creep Data Sheet, No. 43A, National Institute for Materials Science (NIMS), Tsukuba, (2014).
- 15) ASME BPV Code, Section II-D: 2017, SA-213/SA-213M Grade T91.
- 16) The Material Specification in the Technical Regulation of Equipment for Thermal Power Plant, Thermal and Nuclear Power Engineering Society (TENPES), Tokyo, (2016), 160 (in Japanese).
- 17) K. Kimura, K. Sawada and H. Kushima: Advances in Materials Technology for Fossil Power Plants, ed. by D. Gandy *et al.*, ASM International, Materials Park, OH, (2011), 732.
- 18) K. Kimura and Y. Takahashi: Proc. ASME 2012 Pressure Vessels and Piping Conf. (PVP2012), ASME, New York, (2012), PVP2012-78323.
- 19) A. Matsuzaki, Y. Saito, O. Watanabe, C. Shiga and I. Nakagawa: *Tetsu-to-Hagané*, **76** (1990), 1108 (in Japanese).
- 20) M. Yoshino, Y. Mishima, Y. Toda, H. Kushima, K. Sawada and K. Kimura: *ISIJ Int.*, **45** (2005), 107.
- 21) S. Obara, T. Wakai, T. Asayama, Y. Yamada and T. Nakazawa: *Tetsu-to-Hagané*, **95** (2009), 417 (in Japanese).
- 22) K. Maruyama, J. Nakamura, N. Sekido and K. Yoshimi: *Mater. Sci. Eng. A*, **696** (2017), 104.
- 23) K. Kubushiro, Y. Sakakibara and T. Ohtani: *J. Soc. Mater. Sci. Jpn.*, **64** (2015), 106 (in Japanese).