Influence of Chemical Composition and Heat Treatment on Long-term Creep Strength of Grade 91 Steel

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Abstract

Long-term creep strength of ASTM/ASME Grade 91 steels was investigated. Two heats of Grade 91 steels indicated lower creep rupture strength than the other four heats from short-term to long-term, and presence of delta ferrite phase was observed. In the short-term, no difference in creep rupture strength was observed among four heats of Grade 91 steels, however, the large heat-to-heat variation of creep rupture strength was observed in the long-term at 600°C. The higher nickel containing heat indicates lower creep rupture strength in the long-term at 600°C, although nickel concentration was 0.28mass% in maximum. Homogeneously recovered subgrain structure was observed on the specimens creep ruptured after about 80,000h at 600°C for both high nickel low strength heat and low nickel high strength one. Only a small number of fine MX carbonitride particles with a large number of coarse Z-phase were observed on the creep ruptured specimen of high nickel low strength heat, in contrast to low nickel high strength heat in which many MX particles were still observed and Z-phase formation was not pronounced. The difference in stability of fine MX carbonitride particles during creep exposure at the elevated temperatures is a cause of heat-to-heat variation of long-term creep strength of the steels. Decrease in phase transformation temperature of Ac1 with increase in nickel content may reduce stability of the precipitates at the elevated temperatures. Nickel content should be reduced in order to suppress a large drop in long-term creep strength of Grade 91 steel.

Keywords: Creep; grade 91 steel; delta ferrite; nickel; Z-phase

1. Introduction

Creep strength enhanced ferritic (CSEF) steels are one of the key materials for modern power plants because of excellent high temperature strength property and those have contributed to improve energy efficiency of power plants by increasing steam temperature [1]. Those have been widely used as high temperature structural components such as header, main/reheat steam pipes and heat exchanger tubes in Ultra Supercritical (USC) power plant and heat recovery steam generator (HRSG) of combined cycle thermal power plant. CSEF steels...
are strengthened by precipitation of fine MX carbonitrides particles, solid solution strengthening of molybdenum and/or tungsten with a tempered martensitic microstructure.

However, a risk of overestimation of long-term creep strength has been pointed out on those steels [2]. According to difference in microstructural change in the high- and low-stress regimes which derive degradation during creep exposure, a region splitting analysis method was proposed for creep rupture life assessment and prediction of CSEF steels [3]. Reevaluation of long-term creep rupture strength of CSEF steels has been conducted in Japan by means of region splitting analysis method [4-7]. Allowable tensile stress of the CSEF steels regulated in Japanese standard has been revised [8] and guideline of creep life evaluation has been developed on base material and welded joints of CSEF steels [9]. However, experimental data on long-term creep was insufficient to evaluate long-term creep rupture strength of the CSEF steels precisely, therefore, a successive reexamination of long-term creep strength was recommended. Reevaluation of long-term creep strength of Grade 91 steel has been reported by Cipolla and Gabrel [10], and Bendick et al. [11] as a new assessment by European Creep Collaborative Committee (ECCC) in 2009. In this study, heat-to-heat variation of creep rupture strength was investigated on ASTM/ASME Grade 91 steels in consideration of chemical composition and heat treatment condition.

2. Experimental procedures

Creep test data of three heats (MGA, MGB and MGC) of ASTM A213/A213M Grade T91 and three heats (MgA, MgB and MgC) of ASTM A387/A387M Grade 91 plate were investigated. Chemical composition, product form, dimension and heat treatment condition of the steels have been described in the NIMS Creep Data Sheets [12, 13]. MgA and MgB heats are identical except for a holding time of stress relieving heat treatment. Creep tests were conducted in air under constant load using specimens with 6mm diameter and 30mm gauge length for Grade T91 and 10mm diameter and 50mm gauge length for Grade 91 plate steels.

3. Results and discussion

3.1. Creep strength properties

Stress vs. time to rupture curves of the Grade 91 steels are shown in Fig.1. Slope of the curves becomes steeper with decrease in stress, and remarkable drop in creep rupture strength is recognized in the long-term close to 100,000 h at 600 and 650°C. Creep rupture strength of MgA and MgB heats is lower than the other four heats from short-term to long-term over a range of temperatures from 550 to 650°C. In the short-term, no difference in creep rupture strength is observed among four heats of Grade 91 steels except MgA and MgB heats, however, the large heat-to-heat variation of creep rupture strength is recognized in the long-term at 600°C.

Stress vs. minimum creep rate curves of the Grade 91 steels are shown in Fig.2. A large stress dependence of the minimum creep rate with a stress exponent n value of about 20 in the high-stress regime at 550°C decreases with not only increase in temperature to about 10 at 650°C, but also decrease in stress to about 3 in the low-stress regime. Although minimum creep rate of the two heats of MgA and MgB is slightly larger than the others, stress dependence of the minimum creep rate of the steels is essentially the same each other. This change in stress exponent value corresponds to bending of stress vs. time to rupture curves shown in Fig.1. However, large heat-to-heat variation observed in long-term creep rupture strength at 600°C is not recognized on the minimum creep rate.
Fig. 1. Stress vs. time to rupture curves of the Grade 91 steels. Fig. 2. Stress dependence of minimum creep rate of the Grade 91 steels.

3.2. Influence of initial microstructure

Creep rate vs. time curves of the three heats of Grade 91 plate steels at 550°C-200MPa and 650°C-40MPa are shown in Fig.3. Only a creep test of MgC heat at 650°C-40MPa is still in progress. Under the condition of 550°C-200MPa, creep rate of MgA and MgB heats is higher than that of MgC heat from the beginning of creep test and creep rate vs. time curves of the steels in both logarithmic scales are almost parallel in the transient creep stage. On the other hand, creep rate in the transient creep stage of three heats at 650°C-40MPa is almost the same, MgA and MgB heats indicate higher minimum creep rate than that of MgC heat in the shorter time and time to rupture of MgA and MgB heats are shorter than that of MgC heat in both creep test conditions. Lower creep rupture strength of MgA and MgB heats as shown in Fig.1 is considered to be caused by lower creep resistance and the difference in creep strength of the three heats decreases after long-term creep exposure.

Fig. 3. Creep rate vs. time curves of the steels at (a) 550°C-200MPa and (b) 650°C-40MPa.

Optical micrographs at the center of thickness of Grade 91 plate steels after stress relieving heat treatment are shown in Fig.4. Horizontal axis of the micrographs is parallel to the rolling direction. A certain amounts of
delta ferrite phase with an elongated shape along rolling direction is observed on MgA and MgB heats, however, it is scarcely observed on MgC heat. Lower creep strength of MgA and MgB heats is considered to be caused by delta ferrite, since recovery of tempered martensitic microstructure is promoted [14]. Normalizing heat treatment of MgA and MgB heats was conducted at 1050°C and it was enough to obtain an austenite single phase, however, time of normalizing heat treatment of those plate steels with 25mm thickness was only 10 minutes, in contrast to 90 minutes at 1060°C of MgC heat. Hold time for normalizing heat treatment is not regulated in the Codes [8,15,16], however, hold time of one hour for up to one inch thick material has been recommended by Sikka [17].

Fig. 4. Optimal micrographs at the center of thickness of the Grade 91 plate steels after stress relieving heat treatment condition.

Consequently it has been speculated that normalizing heat treatment of MgA and MgB heats was insufficient to obtain a whole martensite microstructure and it reduced creep strength of those heats. In order to obtain sufficient creep strength with a whole martensite microstructure, not only temperature, but also hold time of heat treatment should be considered.

3.3. Microstructural evolution during creep exposure

Creep rupture strength at 1,000, 10,000, 30,000 and 100,000 hours at 600°C of MGA, MGB, MGC and MgC heats of the steels has been estimated by interpolation and/or extrapolation of creep rupture data and shown in Fig.5 as a function of nickel content. Those creep rupture strength has been evaluated by interpolation of the creep rupture data except for 100,000 hours creep rupture strength which has been estimated by extrapolation of the creep rupture data and, therefore, described by dotted line. Creep rupture strength at 1,000 hours of the steels are almost the same independent of nickel content, however, 10,000 and 30,000 hours creep rupture strength tends to decrease with increase in nickel content. Estimated 100,000 hours creep rupture strength at 600°C decreases monotonously with increase in nickel content and those values are lower than 90MPa even in the low nickel content which has been reported as 100,000 hours creep rupture strength of Grade 91 steel at 600°C by European Creep Collaborative Committee (ECCC) in 2009 [18]. Although 100,000 hours creep rupture strength was estimated by extrapolation of creep rupture data, the longest creep rupture data at 600°C of the steels are in a range of 78,000 to 92,000 hours for each heat and, therefore, prediction accuracy of 100,000 hours creep rupture strength is regarded as high enough to reveal the nickel dependence of long-term creep rupture strength.

Creep rate vs. time curves of the Grade T91 steels at 600°C and 80MPa are shown in Fig.6. Creep rate in the transient creep stage up to about 10,000 hours and minimum creep rate are almost the same each other, however, high nickel heat of MGC indicates rapid increase in creep rate after showing minimum value. Nickel is considered to promote remarkable drop of creep rupture strength in the long-term and to provide large heat-to-heat variation of long-term creep rupture strength [19,20].
Bright field TEM images of the MGC heat of Grade T91 steel creep ruptured after (a) 34,141.0h and (b) 80,736.8h at 600°C under stress of 100MPa and 70MPa, respectively are shown in Fig.7. In the specimen creep ruptured after 34,141.0h at 600°C-100MPa, preferentially recovered area is observed along a prior austenite grain boundary. On the other hand, recovery has already extended overall grain interior and grain interior is fully covered by equiaxed subgrains in the specimen creep ruptured after 80,736.8h at 600°C-70MPa. Remarkable drop of creep rupture strength in the long-term is considered to be caused by progress of recovery whole area of grain interior.

Change in hardness of the MGC heat with increase in creep exposure time at 600°C and 70MPa is plotted by open symbol in Fig.8 together with the hardness in the gauge and grip portions of the creep ruptured specimens plotted by solid symbols [21]. Large reduction of hardness after creep rupture is observed in the gauge portion of the creep ruptured specimens and those values are considerably lower than the initial value of HV235 in the as tempered condition. On the other hand, hardness in the grip portion of the creep ruptured specimens is slightly lower than that of the virgin material. This large difference in hardness between gauge and grip portions of the creep ruptured specimen indicates that microstructural change during creep exposure is promoted in the gauge portion by stress. For the crept specimens interrupted prior to creep rupture, hardness
change is almost the same as that in the grip portion of the creep ruptured specimens up to about 30,000 hours. However, remarkable drop in hardness is observed with increase in creep exposure time in excess of 30,000 hours. It has been considered that significant change in microstructure takes place after creep exposure for 30,000 hours.

![Fig. 8. Hardness change of MGC heat of the Grade T91 steel during creep exposure.](image)

The changes in mean subgrain size and dislocation density during creep exposure at 600°C-70MPa are plotted as a function of creep exposure time and shown in Fig.9 [21]. For measuring of dislocation density, ten different areas were investigated for each sample. A mean subgrain size gradually increases with increase in creep exposure time up to 70,000 hours, and it indicates remarkable increase in excess of 70,000 hours. A mean dislocation density decreases to about half during creep exposure for about 30,000 hours. Magnitude of change in mean dislocation density is relatively small during creep exposure from 30,000 hours to 70,000 hours, however, it decreases significantly in excess of 70,000 hours up to creep rupture. Subgrain boundaries retard dislocation motion during creep deformation [22]. Growth of subgrain reduces total area of subgrain boundaries and may lead to decrease in creep resistance. Coarsening of subgrain and decrease in dislocation density are considered to have an influence on the onset of accelerating creep. With increase in creep exposure time from 30,000 to 50,000 hours, hardness decreases remarkably as shown in Fig.8, however, magnitude of changes in subgrain size and dislocation density in the same time range is very small, and significant change in those are observed in excess of 70,000 hours. Consequently, remarkable decrease in hardness is considered to be caused by changes in precipitates rather than dislocation structure. It has been reported that M23C6 and MX particles can affect the hardness [23], since they may obstruct dislocation motion during hardness measurements.

![Fig. 9. Changes in (a) mean subgrain size and (b) mean dislocation density of MGC heat of the Grade T91 steel during creep exposure at 600°C and 70MPa.](image)
Changes in number density of MX and Z-phase particles in MGC heat with increase in creep exposure time at 600°C and 70MPa are shown in Fig. 10 [21]. The number density of MX corresponds to a total number density of VX and NbX particles. Nucleation of Z-phase was recognized after creep exposure for 10,000 hours and the number of Z-phase particles gradually increased with increase in creep exposure time. Number density of MX particles is almost constant up to about 30,000 hours, however, it decreases during creep exposure in excess of 30,000 hours and that in the creep ruptured specimen is less than one tenth of that in the as tempered condition. In the specimen creep ruptured after 80,736.8 hours, number density of MX and Z-phase particles are almost the same. It has been reported that decrease in mean diameter of MX particles during creep exposure is caused by formation of Z-phase particles on 11Cr steel [24]. The precipitation of Z-phase takes place as a consumption of MX particles. Decrease in number density of MX particles in excess of 30,000 hours reduces creep resistance, as well as remarkable drop in hardness, since MX particles are dominant strengtheners of Grade 91 steel. Consequently, it has been concluded that remarkable drop of creep rupture strength in the long-term is caused by dissolution and decrease in number density of MX carbonitrides particles.

Large heat-to-heat variation arising in the long-term is considered to be caused by nickel, since nucleation and growth of Z-phase is promoted by nickel [19], as well as coarsening of precipitates [20]. Decrease in phase transformation temperature of Ac1 with increase in nickel content may reduce stability of the precipitates at the elevated temperatures. Although precise mechanism of influence of nickel on precipitation sequence during creep exposure is not yet clearly understood, nickel content which is regulated as 0.40 mass% in maximum in the current codes [9,15,16] should be reduced in order to suppress a large drop in long-term creep strength of Grade 91 steel.

Fig. 10. Changes in number density of MX and Z-phase particles during creep exposure of the MGC heat of Grade T91 steel at 600°C and 70MPa.

4. Conclusions

Lower creep rupture strength of MgA and MgB heats was considered to be caused by presence of delta-ferrite which was derived from insufficient normalizing heat treatment. In order to obtain sufficient creep strength with a whole martensitic microstructure, not only temperature, but also hold time of heat treatment should be considered.

In the short-term, no difference in creep rupture strength was observed among four heats of Grade 91 steels except MgA and MgB heats, however, the large heat-to-heat variation of creep rupture strength was recognized in the long-term at 600°C. Good correspondence between long-term creep rupture strength and nickel content was observed, and long-term creep strength of the Grade 91 steel decreased with increase in nickel content.

During creep exposure at 600°C and 70MPa, remarkable drop in hardness was observed with increase in creep exposure time in excess of 30,000 hours, in accordance with acceleration of creep rate. Decrease in number density of MX carbonitrides particles was observed concurrently with nucleation and growth of Z-
phase. It has been concluded that remarkable drop of creep rupture strength in the long-term is caused by dissolution and decrease in number density of MX carbonitrides particles.

Large heat-to-heat variation arising in the long-term is considered to be caused by a difference in nickel content, since nucleation and growth of Z-phase is promoted by nickel, as well as coarsening of precipitates, and nickel content should be reduced in order to suppress a large drop in long-term creep strength of Grade 91 steel.

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References

[18] ECCC Data Sheets, Steel Grade 91 (X10CrMoVNb9-1), (2009).