1. Introduction

Power plants with a high thermal efficiency are needed to reduce CO₂ emissions. High chromium (9–12% Cr) ferritic steels with tempered martensite are used for boilers and steam turbines in power plants because of their good creep resistance, large thermal conductivity and low coefficient of thermal expansion which suppresses thermal stress. The steels need to have better creep strength to increase the steam temperature and pressure, which contributes to improving thermal efficiency.

Recently, we have reported 1) that extremely low carbon (ELC) 9Cr ferritic steel (9Cr–3W–0.2V–0.06Nb–3Co–0.05N–B) exhibits a much higher creep strength than 9Cr–0.5Mo–1.8W–VNbN (ASME-P92) steel. By reducing the carbon content of ferritic steel, not the M₂₃C₆ carbides but only fine MX nitrides precipitate along lath, block, packet and prior austenite grain boundaries as well as in the matrix during tempering. 2) The fine MX nitride can pin the boundaries during long term creep deformation since the growth rate of the MX nitride is much lower than that of the base steel. The presence of large Cr₇N particles after tempering and the higher coarsening rate of the MX nitride in the high nitrogen steels cause an increase in mean inter-particle spacing on boundaries, leading to a decrease in creep strength. The Z phase formation was observed after creep exposure in the gauge portion of all the steels. The Z phase formation in the high nitrogen steels occurs at relatively short term in contrast to the base steel. The short term precipitation of the Z phase in high nitrogen steels can contribute to a decrease in creep strength since the Z phase forms at the expense of the MX nitride which is a main strengthening obstacle.

KEY WORDS: low carbon 9Cr steel; creep resistance; precipitation reaction; coarsening of MX nitride.

Effect of Nitrogen Content on Microstructural Aspects and Creep Behavior in Extremely Low Carbon 9Cr Heat-resistant Steel

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Effects of nitrogen content on microstructure and creep strength in extremely low carbon 9Cr ferritic steel were investigated, focusing on the dislocation structure and the distribution of precipitates. The creep strength of the high nitrogen steels was lower than that of the base steel, even though the initial lath width and prior austenite grain size in the high nitrogen steels are finer and larger, respectively. MX nitrides as well as large Cr₇N particles were distributed along lath, block, packet and prior austenite grain boundaries in the high nitrogen steels after tempering. The large particles occupy the MX nitride precipitation sites. The coarsening of the MX nitride during creep exposure in the high nitrogen steels was faster than that of the base steel. The presence of large Cr₇N particles after tempering and the higher coarsening rate of the MX nitride in the high nitrogen steels cause an increase in mean inter-particle spacing on boundaries, leading to a decrease in creep strength. The Z phase formation was observed after creep exposure in the gauge portion of all the steels. The Z phase formation in the high nitrogen steels occurs at relatively short term in contrast to the base steel. The short term precipitation of the Z phase in high nitrogen steels can contribute to a decrease in creep strength since the Z phase forms at the expense of the MX nitride which is a main strengthening obstacle.

KEY WORDS: low carbon 9Cr steel; creep resistance; precipitation reaction; coarsening of MX nitride.
increase of the N content on the precipitation behavior of MX nitrides and creep strength in ELC 9Cr ferritic steel.

2. Experimental Procedure

Chemical compositions and heat treatment conditions of the steels examined are given in Table 1. The steels were melted as 50 kg-ingots in a vacuum induction furnace and forged into bars with a diameter of 25 mm. The 5N steel is the base material reported in our previous works, and the 7N and 10N steels have a higher N content than the base material. The undissolved MX nitrides were not observed in the 5N steel after normalizing at 1373 K. According to the extracted residue analysis for 7N and 10N steels, about 0.02 to 0.04 mass% of V and Nb was observed as undissolved MX nitrides after normalizing at 1373 K. The amount of V and Nb in undissolved MX nitrides for both steels was around 0.005 to 0.01 mass% after normalizing at 1473 K. Normalizing for the 7N and 10N steels was done at a higher temperature than the 5N steel to reduce the undissolved MX nitrides. Several tempering temperatures were selected to control hardness. The microstructure of the steels was a tempered martensite after the heat treatment. Vickers hardness for the 5N, 7N and 10N steels was HV230, HV223 and HV232, respectively. Creep tests were performed at 923 K under constant load in air, using specimens of 10 mm in gauge diameter and 50 mm in gauge length. The amount of precipitates was estimated by the quantitative analysis of extracted residues. Specimen microstructures were observed using a conventional TEM and an energy-filtered TEM (EF-TEM) at 200 kV. Thin foil and extracted carbon replica were prepared for TEM observation. Precipitate compositions were analyzed by an energy dispersive X-ray spectrometer (EDS). Lath width and dislocation density were measured. The mean radius of MX nitride was evaluated by taking 10 bright field images with the TEM, corresponding to about 450 particles per specimen.

3. Results and Discussion

3.1. Effect of Nitrogen Content on Creep Strength

Figure 1 shows the applied stress and rupture time diagram of the steels studied. The creep life of the 7N and 10N steels is shorter than that of the 5N steel. This tendency can be seen even within a short term region, indicating that the initial microstructure is different among the steels. The creep life is related to both creep resistance and the fracture process. The relationship between minimum creep rate and applied stress is shown in Fig. 2. The minimum creep rate for the 7N and 10N steels is higher than that for the 5N steel, indicating that the difference of the creep resistance contributes to the difference of creep life.

3.2. Initial Dislocation Structure

Figure 3 shows a dislocation structure of the steels before creep. All the steels have a typical tempered martensite with a high dislocation density. Mean lath width, dislocation density and prior austenite grain size for the 5N, 7N and 10N steels are listed in Table 2. The prior austenite grain size for the 7N and 10N steels is larger than that of
the 5N steel due to their higher normalizing temperature. The lath width for the 5N steel is larger than that of the 7N and 10N steels. It has been reported that although prior austenite grain size affects packet size in carbon steel, the lath width does not depend on prior austenite grain size.9) The higher tempering temperature of the 5N steel shown in Table 1 can contribute to the larger lath width since the lath width increases during tempering.10) The dislocation density is not different among these steels. It can be predicted from the initial microstructure that the creep strength of 7N and 10N steels is higher than that of the 5N steel since the 7N and 10N steels have a finer lath and a larger grain size.11–13) However, the creep strength for the steels shows opposite tendency as shown in Fig. 2. Other microstructural factors than the initial dislocation structure and grain size should be considered in order to explain the difference in creep strength. The degradation behavior of the dislocation structure during creep exposure affects creep strength.12) Precipitation behavior should be investigated since the pinning of precipitates retards the recovery of dislocation structure during creep exposure.12,14)

### 3.3. Effect of Nitrogen Content on Precipitation Behavior

Figure 4 shows the distribution of precipitates before creep for an extracted carbon replica. Most of precipitates in the 5N steel are MX nitrides.2) The MX nitrides are distributed along boundaries such as block and prior austenite grain boundaries. The MX particle distribution in the 7N and 10N steels is the same as that of the 5N steel. The V content of the 5N steel in extracted residue is about 0.1 mass% after tempering.2) The V content of the 7N and 10N steels in extracted residue was about 0.15 mass% after tempering, indicating that an increase in N content can contribute to the dispersion of more MX nitrides. However, in the 7N and 10N steels, relatively large particles are also present along boundaries in contrast to the 5N steel as shown in Figs. 4(b) and 4(c). Energy filtered images of V and Cr in extracted carbon replica are shown in Fig. 5. The elemental maps of V and Cr show the precipitate distribution. The high contrast particles in the V map are the MX nitrides since MX nitride consists of V, Nb and N. Relatively large particles are seen in the Cr map for 7N and 10N steels. The large particles in the Cr map are not M23C6 since the steels contain extremely low carbon. It was confirmed by EDX analysis that the mean content of Cr in the large particles was about 88 mass% for both steels. The Cr-rich particles are CrN as reported in the other type of high nitrogen steel.15) The pinning effect of MX nitride on boundaries such as lath, block and prior austenite grain boundaries contributes to the improvement of creep strength for the 5N steel. The CrN particles are not found in the 5N steel, however, several CrN particles are distributed after tempering in the 7N and 10N steels. The CrN particles occupy MX nitride precipitation sites as shown in Figs. 4 and 5, leading to an increase in mean inter-particle spacing on the boundaries before creep. The increase can cause a decrease in creep resistance.16) The coarsening of the CrN during creep exposure in 10N steel is shown in Fig. 6. The CrN rapidly coarsens after creep exposure, indicating that the mean inter-particle spacing on boundaries rapidly increases. The pinning effect of CrN on the boundaries is much lower than that of MX nitride due to its higher coarsening rate.17) The increase in mean inter-particle spac-


\[
\frac{r_m}{r_0} = \frac{k t}{\sigma M_{AB} V D u_{\text{p}} M} \left( u_{\text{p}} M - u_{\text{M}} M \right) \frac{1}{m - 1}
\]

where \( \sigma \) is the interfacial energy of the carbides, \( V \) is the molar volume of the carbides, \( D \) is the lattice diffusion coefficient of M atom, \( u_{\text{M}} \) and \( u_{\text{p}} \) are the concentration of M atoms in the matrix and carbides, respectively. Figure 8 shows the mean composition of metallic elements in MX nitride before creep. 10–20 particles along boundaries were analyzed by EDX per specimen. The MX nitrides of all the steels contain V, Nb, Cr and Fe. The amounts of Cr and Nb for the 7N and 10N steels are larger and smaller than those of the 5N steel, respectively. Applying Eq. (2) to the coarsening of the MX nitride, M atoms will be mainly V. The value \( u_{\text{p}} \) is the same among the steels as shown in Fig. 8. The value \( u_{\text{M}} \) for the 5N steel after tempering is larger than that of the 7N and 10N steels since the amount of V is the

Fig. 5. Energy filtered images of Cr and V after tempering in extraction replica. (a)–(c) V map, (d)–(f) Cr map. (a), (d) 5N steel, (b), (e) 7N steel, (c), (f) 10N steel.

Fig. 6. Energy filtered images of Cr in extraction replica of the 10N steel. (a) after tempering, (b) after crept for 3001 h at 923 K.

Fig. 7. Change in MX nitride size during creep exposure at 923 K.
same among the steels listed in Table 1 and the V content (0.1 mass%) in the extracted residue of the 5N steel is lower than that (0.15 mass%) of the high nitrogen steels. The equation then gives the rate constant $k$ of the 5N steel to be higher than that of the high nitrogen steels. However, the tendency of the MX coarsening is opposite as shown in Fig. 7. Hirata et al.\textsuperscript{21} reported that the coarsening rate of MX (VC) which contains large amount of Cr is higher than that of MX in which M atoms is mainly V in simulated HAZ specimens of high Cr ferritic steel. They explained that the higher coarsening rate of the VC is originated from lattice diffusion control of Cr. The diffusion of Cr may affect the coarsening of MX nitrides in the high nitrogen steels since the MX in the 7N and 10N steels contains large amount of Cr in contrast with the 5N steel. However, the mechanism for the higher coarsening rate of the MX nitride in high nitrogen steels is not clear at present.

Consequently, the presence of large Cr$_2$N particles after tempering and the higher coarsening rate of the MX nitride cause a decrease in creep strength of the high nitrogen steels.

3.4. Change in Precipitates During Creep Exposure

It was seen that Laves phase precipitation occurs during creep exposure in all the steels. However, the precipitation behavior was the same for all the steels.

It was confirmed by EDX analysis that particles except the Cr$_2$N and Laves phase in which the composition of the metallic element was different from that of the MX nitride were present in the gauge portions of the 5N, 7N and 10N steels ruptured for relatively long time. Figure 9 shows mean compositions for the metallic elements in the particles after creep exposure. 10 to 25 particles were analyzed by EDX per specimen. The mean composition of metallic elements in MX nitride is also shown in the figure. Unknown particles contain the same metallic elements as the MX nitride. However, the Cr content of the particles is much larger than that of the MX nitride. This suggest that the Cr-rich particles are Z phase since the average Cr content in 38 to 45 mass% in the Z phase as reported in the other type of high Cr steels.\textsuperscript{22–25} Figure 10 shows TEM images of the 7N steel. Z phase was identified by selected area electron diffraction, using a tetragonal unit cell with $a=0.286$ nm and $c=0.739$ nm reported by Strang et al.\textsuperscript{22} In the case of 7N and 10N steels, the Z phase was seen in the specimens ruptured for a relatively short time as shown in Fig. 9, although other researchers\textsuperscript{22–25} found the Z phase in specimens ruptured after a long term, more than 5000 h. If the MX nitride changes to the Z phase during creep deformation, relatively high Cr content in the MX nitride of the 7N and 10N steels in contrast to the 5N steels would accelerate the Z phase formation. Furthermore, it has been reported that the Cr$_2$N would directly change to the Z phase after creep exposure in 11Cr–Mo–W–VNbN steel.\textsuperscript{26} The Z phase can quickly form in the 7N and 10N steels since the
Cr$_2$N precipitates after tempering in the steels. The Z phase precipitation can cause creep strength degradation since the formation of the Z phase occurs at the expense of the MX nitride pinning lath, block, packet and grain boundaries during creep exposure.\textsuperscript{23,27} It can be predicted that the short term precipitation of the Z phase in the 7N and 10N steels contributes to a decrease in creep strength for the steels.

The changes in the amount of V and Nb in extracted residue during creep exposure are shown in Fig. 11. The extracted residue was obtained from the gauge portion of the specimens. The Nb content does not change during creep in all the steels. The V content in the 7N and 10N steels is almost constant during creep exposure, indicating that the Z phase formation during creep is caused by the expense of the MX nitride since the Z phase contains V. However, the V content in the 5N steel increases during creep exposure. This suggests that additional VN formation occurs during creep since most of the Nb is spent to form precipitates before creep as shown in Fig. 11. Additional Z phase formation without the expense of the MX nitride cannot occur since the Z phase formation needs Nb. The additional VN formation during creep exposure would contribute to the lower coarsening rate of the MX nitride in the 5N steel shown in Fig. 7. The Cr content in extracted residue increased during creep exposure. However, it is difficult to detect the Z phase formation by monitoring change of the Cr content during creep since the Laves phase which contains Cr also precipitates during creep exposure. A quantitative analysis of the microstructure is needed to clarify the effect of the Z phase formation on creep strength in detail.

4. Conclusions

Effects of increased nitrogen content on creep strength and precipitation behavior in ELC 9Cr ferritic steel 0.002C–9Cr–3W–VNbCo–0.05N–B were investigated. The results are summarized as follows.

1) An increase in nitrogen content decreases the creep resistance of the base material 0.002C–9Cr–3W–VNbCo–0.05N–B, leading to shorter creep life, even though the high nitrogen steels have finer lath and larger prior austenite grain after tempering.

2) The relatively large Cr$_2$N particles were observed in high nitrogen steels 0.002C–9Cr–3W–VNbCo–(0.074, 0.103)N–B after tempering. The particles occupy the part of precipitation site of MX nitride which is the main strengthening factor, indicating an increase of mean inter-particle spacing of the MX nitride and Cr$_2$N on boundaries such as lath, block, packet and prior austenite grain boundaries. This contributes to the decrease of creep strength for high nitrogen steels.

3) The coarsening rate of the MX nitride was higher in the high nitrogen steels, leading to an increase in mean inter-particle spacing of the MX nitride during creep exposure. This contributes to the decrease in creep strength. The mechanism of higher coarsening rate of the MX nitride in the high nitrogen steels is not clear at present.

4) The Z phase was observed in the base material after creep exposure for about 10 000 h and high nitrogen steels after creep exposure for 1 000 to 3 000 h. The short term precipitation of the Z phase can contribute to lower creep strength of the high nitrogen steels since the Z phase forms at the expense of the MX nitride.

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