Effects of Nitrogen in 9Cr–3W–3Co Ferritic Heat Resistant Steels Containing Boron

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Many researchers revealed that the addition of small amount of boron (B) significantly improves the creep strength of ferritic heat resistant steels. However the mechanism for such an effect caused by B has not been clarified yet. In the present study, the effect of nitrogen (N) on the behavior of B in 9Cr–3W–3Co base steels was examined using Alpha-particle Track Etching (ATE), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and creep test. It was confirmed that creep lives have significantly increased by lowering the N content in boron containing steels. The prediction of creep life using Larson–Miller parameter suggests that high N–high B steel shows lower creep strength compared with high N–low B, low N–low B and low N–high B steels. SEM showed that B increases the precipitates stability against coarsening. TEM revealed that the stability of the matrix against recovery reaches maximum in low N–high B steels, while this stability is very weak in high N-high B steel. ATE showed that B segregating along packet and block boundaries and free B homogeneously distributing in the matrix are more effective on strengthening than B contained in M23C6 carbides. In addition, B in steels of a suitable content of N is contributable to the enhancement of creep strength through increasing the amount and the stability of fine precipitates such as VN. High content of N is expected to reduce such effects of B probably through the precipitation of BN, although no experimental evidence has been obtained.

KEY WORDS: heat resistant steel; boron; nitrogen; creep strength; microstructure; alpha particle track etching.

1. Introduction

Improving the plant’s thermal efficiency increases the economic utilization of fossil fuels and thereby reduces both the plant-life time costs and the release of SO2, NOx and CO2 emissions. The key technology of an increase in steam conditions for steam power system is to provide better heat resistant materials. Modified 9 to 12% Cr ferritic heat resistant steels have been developed for applications in ultra-super critical (USC) power plant technology for future power generation. In these steels boron (B) is thought to be a very effective element to enhance the creep strength. 1–3) A number of fundamental researches have been carried out to reveal the strengthening mechanisms by B. Takahashi and Fujita4) examined the effect of B addition on the strength of 10.5%Cr–1.5Mo–V–Nb steel and the micro-structure at elevated temperatures, and the following points were reported: 1) In B containing steels, the width of precipitation free zone along grain boundary is narrowed, 2) Boron addition delays the transition of M23C6→M7C3, 3) No boride can be observed, 4) Boron substitutes for carbon in M23C6 and forms M23(B,C)6, and 5) The coarsening of M23(C,B)6 is delayed compared with M23C6. Harada et al.5) observed in 11Cr–0.2Mo–2.7W–VNb–0.02B steel that B existed in precipitate which existed along the prior austenite grain boundary and contained W, Fe, and Cr, whereas B did not exist in the matrix and precipitates in the grain. They thought that the suppression of grain boundary sliding due to such grain boundary precipitates containing B contributes to strengthening. In alpha-particle track etching (ATE) micrographs shown by Tamehiro et al.,6) however, B seems to exist also in the matrix before and after aging. Muraki et al.7) examined the behavior of B using ATE and other techniques and thought that the effect of B on refining and stabilizing of precipitates in the grain and along the grain boundaries contribute to the creep strength. Azuma et al.8) observed that the solution temperature of Nb– and V–carbides moves to higher temperature by B and thought that stabilizing of MX type carbides by B was one of reasons for strengthening by B. Lundin et al.9) and Murayama et al.10) indicated using AP-FIM that very fine precipitates containing V exists in B containing high Cr steel. Park et al.11) insisted that the precipitation of fine V(C,N) is most important for strengthening of ferritic heat resisting steels. Moreover, Uchida et al.12) observed that the recovery proceeded rapidly after the ending of the precipitation of fine V(C,N) in 10Cr–1.5Mo–V–Nb steel. These experimental results8–12) indicate that the effect of B on the precipitation of fine V(C,N) is closely related to the increase in creep strength. On the other hand, Abe et al.13) studied the effect of B on 9Cr–3W–3Co steel using FE-AES. They reported that B improved the stability of microstructure through the
stabilization of M$_2$3C$_6$ carbides and B suppressed the coarsening of M$_2$3C$_6$ carbides by enriching into them.

As shown above, irrespective of the number of researches, the details of the creep strengthening mechanism by B addition have not yet been clear. In addition, some experimental data show that strengthening by B disappears in steels of a relatively high content of N but the reason has not been clarified. Considering above background, this paper aims to give a broad characterization of the B behavior during heat treatment and creep of 9Cr–3W–3Co steels with two levels of N content using ATE, SEM and TEM.

2. Experimental Work

The chemical compositions of the steels used are given in Table 1. These steels were prepared by vacuum melting, hot forging at 1423 K and hot rolling at 1423 K to plates of 15 mm thickness. Then normalizing was carried out at 1050°C for 1 h for all steels followed by tempering at 780°C for 2 h (Steels B1 and B2) and at 580°C for 10 h followed by 710°C for 20 h (Steels B3, B4 and B4-2). Steels B1 and B2 are boiler steels while Steels B3, B4 and B4-2 are rotor steels. Steel B4-2 was prepared additionally due to the shortage of the amount of Steel B4. The heat-treated plates were received from the Japan Steel Works as co-used steels in the research committee of Iron and Steel Institute of Japan on Elucidation of Behavior of Small Amount of Boron in Steel and Promotion of the Usage of Boron, which started in 1999 fiscal year. Blanks were cut for creep tests, observation of B distribution and microstructure and hardness measurement. Other blanks (10/11003/5 mm) were thermal aged at 600°C, 650°C, 700°C for 1, 10 and 100 h to observe B behavior and microstructure change. Creep test was conducted at 650°C under the nominal stress (140, 160 and 200 MPa); and at 700°C under the nominal stress (100 and 140 MPa). SEM and TEM were carried out for as-received and crept samples. The precipitates were characterized by EDS analysis. ATE was carried out for as-received, thermal aged and crept samples. In addition, to eliminate the effect of tempering condition on the B distribution, a heat treatment was carried out for all steels: normalizing at 1050°C for 1 h followed by tempering at 710°C for 2 h using step cooling. This heat treatment will be called a controlled heat treatment in this paper. ATE was carried out for both normalized and tempered conditions and the creep test was conducted again using the controlled heat-treated samples. Irradiation of neutrons for ATE was performed in the reactor JRR-4 at the Japan Atomic Energy Research Institute.

3. Results and Discussion

3.1. Hardness and Creep Strength

Vickers hardness of as received steels and controlled heat-treated steels are listed in Table 2. For as-received steels, Steels B3 and B4 shows higher hardness than Steels B1 and B2, which may be attributed to the lower tempering temperature for Steels B3 and B4. For controlled heat-treated steels, Steel B3 shows the highest hardness while Steel B1 shows the lowest hardness; Steels B3 and B4 shows no major difference from the as-received condition. Prior austenite grain sizes of the as-received steels are tabulated in Table 3. Almost the same prior austenite grain size is obtained for Steels B1 and B3. However Steels B2 and B4 show finer prior austenite grain size, which may be attributed to the high B content. The creep curves for Steels B1 and B2 at 650°C under 160 MPa nominal stress are shown in Fig. 1. It can be seen that increasing the B content in 0.05% N steels significantly decreases creep life. In Steel B1, creep rate in the transient state is lower and the transition from transient to acceleration creep shifts to longer times. Figure 2 shows the creep curves for Steels B3 and B4 at 650°C under 160 MPa nominal stress. It can be seen that increasing the B content in 0.02% N steels significantly increases creep life. Creep rupture strength of Steels B1 to B4-2 and Steel W3 at 650°C is shown in Fig. 3. Steel W3 (0.1C–0.03Si–0.01Mn–0.004P–0.002P–0.002S–9.0Cr–
0.20V–0.05Nb–2.95W–3.06Co–0.05N–free B) is the co-used steel in the past committee of ISIJ on Ferritic Heat Resisting Steels and it is used for comparison with the present series of steels. It can be observed that increasing the B content up to 60 ppm in 0.05% N steels shows remarkably lower creep rupture strength. Increasing the B content in 0.02% N steels, however, shows an inverse effect. At the stress of 140 MPa, creep rupture lives of Steels B1 and B2 are 1660 and 1478 h respectively however the increase of the boron content from 10 to 60 ppm in 0.05% N steels was expected to show longer creep rupture life than found. But Steel B3 and B4-2, which have 0.02% N; show a superior creep life at this stress. Prediction of creep life using Larson–Miller parameter resulted in 10 000 h at 650°C under 100 MPa for Steel B2 and this value is similar to the value of Steel W3 (Fig. 4). Steel B1, B3 and B4, however, shows 21 000, 27 000 and 45 000 h respectively under the same conditions. Due to the difference in tempering condition between boiler (Steels B1 and B2) and rotor (Steels B3, B4 and B4-2) as-received steels, comparison can only be done for the same tempered condition. For boiler steels, increasing the B content from 10 ppm B to 60 ppm at 0.05% N content shows shorter creep rupture time. This implies that the simultaneous addition of B and N is inconvenient in boiler steels. For rotor steels, fixing the N content at 0.02% the creep life increases by increasing the B content. These results consist with the recommendation by Fujita,14) who mentioned that N content must not exceed 0.02% in B added heat resistant steels.

Figure 2. Creep curves of as-received Steels B3 and B4 at 650°C under 160 MPa.

Figure 3. Creep rupture strength of Steels B1–B4, B4-2 (as-received) and W3 at 650°C.

Figure 4. Rupture time as a function of Larson–Miller parameter.

Figure 5. Creep curves of controlled heat-treated Steels B1–B4-2 at 650°C under 160 MPa.

Figure 6. Creep rupture strength of controlled heat-treated Steels B1–B4-2 at 650°C.
3.2. Microstructure

Figure 7 shows the microstructures of as-received steels observed by SEM. All steels are full martensitic and almost the same microstructure is obtained. Figure 8 shows the SEM micrographs of all as-received steels after creep rupture testing at 650°C under 160 MPa. No other precipitates rather than M$_2$C$_6$ and Fe$_2$W were detected by EDS analysis and these precipitates occur along prior austenite grain boundary and inside the grain. This does not mean that M$_2$C$_6$ and Fe$_2$W are the only precipitates in these steels but as it is well known EDS is not sensitive to very fine precipitates like VN and Nb(C, N). Abe et al.\textsuperscript{13} studied the effect of B on 9Cr–3W–3Co steel using FE-AES. They concluded

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Fig. 7. SEM micrographs of as-received steels.

Fig. 8. SEM micrographs of crept specimens (as-received) at 650°C under 160 MPa.
that B improved the stability of dislocation microstructure through the stabilization of M_{23}C_{6} carbides. They thought that this stabilization is attributed to the suppression of the coarsening by B enriched in M_{23}C_{6} carbides. Moreover, Takahashi and Fujita,4) showed a similar results too. In the present study, neither the coagulation tendency nor the coarsening rate can be discussed, as the magnification used in SEM observation was relatively low ×3 000.

Figure 9 shows the TEM of the as-received steels. Lath martensitic structure is obtained for all steels. Steel B2, however, shows the largest lath width, which is about 0.5 μm. So, large lath width and low hardness of Steel B2 may be considered as reasons for the short creep rupture time of this steel observed in the short-term creep test (200, 160 MPa). Figure 10 shows microstructures of the steels crept at 650°C under 160 MPa. Lath–martensitic structure partially disappears and changes to sub-grain structure. The rank of creep rupture lives at 650°C under 160 MPa is B4>B3>B1>B2. When this rank matched with the rate of recovery, it becomes in the order of B2>B1>B3>B4. The lath width, rate of coarsening of precipitates and dislocation density affect the overall level of recovery. Before discussing the ATE results, the basic principles of ATE should be explained. The procedure of ATE is as follows: a) A cellulose film is glued on to the polished surface of the specimen. b) Specimen is irradiated by thermal neutrons; the following fission reaction ^10_B+n→^7_Li+^4_He(α) takes place in the surface layer of the specimen. c) The discharged alpha particles produce tracks in the cellulose film and these tracks density is proportional to the boron content of the specimen. d) The tracks are made visible by etching the cellulose film in aqueous NaOH. So, the black spots correspond to the place where the boron exists, however the black background corresponds to homogeneous distribution of B in the matrix. Figure 11 shows ATE micrographs of the as-received steels. Although there is a homogeneous distribution of B in the matrix (black background) in Steel B4, segregation along grain boundaries was not observed. Noticeable segregation was not observed for Steels B1 to B4 after thermal aging at 600°C, 650°C, 700°C for 1, 10 and 100 h. For specimens crept at 650°C under 160 Mpa, segregation of B along grain boundaries was not observed as shown in Fig. 12. Figure 13 shows ATE micrographs of crept steels at 700°C under 100 MPa, the segregation is occurred along sub-grain boundaries only in Steel 4. These sub-grain boundaries were arrowed. The number density of precipitates containing B (black spots) showed maximum in Steel B2, which shows the shortest creep life. This high density of precipitates remains almost constant up to rupture. This implies that B in precipitates is not the sole mechanism of strengthening in ferritic heat resistant steels. Figure 14 shows the as-normalized ATE micrographs of controlled heat-treated samples. It can be observed that the segregation occurs along prior austenite grain boundaries (black arrows) and ferritic boundaries (gray arrows) in Steels B1 and B3 while the segregation occurs along ferritic grain boundaries only in Steels B2 and B4. But this segregation tends to varnish after tempering and replaced by homogeneous distribution of boron mainly in the matrix as shown in Fig. 15. To explain the reasons for dissipation of B segregation after tempering, the segregation of B should be discussed in more detail. Two kinds of boron segregation occur at austenite grain boundaries. One is the equilibrium type and the other one is the non-equilibrium type. Most of the segregation occurred is composed of superposition of the two types. The characteristics of equilibrium segrega-
tion at grain boundaries during isothermal holding have been extensively investigated while considerably less is known about non-equilibrium segregation during isothermal holding. As the grain boundary segregation builds up above the equilibrium value, reverse diffusion of the boron atoms away from the boundaries takes place and the non-equilibrium segregation is gradually dissipated. In these controlled heat-treated samples, the borides (black...
spots) were observed along prior austenite grain boundaries and inside the grains. The maximum density of borides is obtained also in high B–high N Steel B2 and the difference in precipitate density was small between normalized and tempered steels. This high density of borides occurred in Steel B2 under all heat treatment conditions is attributed to the high contents of B and N. Following Fujita and Hidaka et al., addition of N in B free steels shows remarkably high creep rupture strength, but an inverse effect arises in simultaneous addition of N and B. Ludin et al. studied the type and composition of precipitates in 10% Cr steel using atom probe analysis. They observed the precipi-
tation of $M_23C_6$, MX and $M_6N$, and mentioned that during tempering at 750°C, $M_6N$ precipitates inside the laths, at lath boundaries and along prior austenite grain boundaries. Later during tempering intergranular $M_6N$ dissolves at the same time as $M_23C_6$ is formed. So, if BN is formed in high N–high B steels and it is dissolved at the same time as $M_23C_6$ is formed, then almost all of the B in the steel resides in the $M_23C_6$ and is not much effective to stabilize dislocation microstructure of the matrix. Such phenomena increase the number densities of BN and therefore $M_23(C, B)_6$ and do not increase the strength in high B–high N steels comparing with high B–low N steels, which is consistent

Fig. 14. ATE micrographs of controlled heat-treated steels after normalizing.

Fig. 15. ATE micrographs of controlled heat-treated steels after tempering.
with the observation of the present paper. But there has been so far no report, which observes BN in this kind of high Cr heat resistant steel and detects the nucleation of $M_23(C, B)_6$ on BN.

Another explanation for the effect of N on B behavior and creep strength is as follows. Boron plays a role to increase an amount of very fine precipitates like VN or V(C, N) and contributes to increasing creep strength as indicated before.\(^8\)\(^{-12}\) If BN is formed in high N–high B steels, and the amount and the stability of such fine precipitates are reduced, creep strength decreases. This explanation is more attractive than the explanation based on the effect on $M_23C_6$. Because the effect of $M_23C_6$ or $M_23(C, B)_6$ on the stabilization of dislocation microstructure and creep strength is thought to be much smaller than that of very fine precipitate like VN or V(C, N). But also in this explanation, there has been no experimental support showing the precipitation of BN. To detect the precipitation of BN is future work, although even if BN precipitates in this kind of steels, it seems to be difficult to detect it when the dissolution and the change to another precipitate occur as mentioned by Ludin et al.\(^9\)

4. Conclusions

Boron behavior and its effects on creep strength and microstructure of 9Cr–3W–3Co heat resistant steels were investigated at N contents of 0.02 and 0.05%. The results can be summarized as follows.

(1) For as-received steels, increasing the B content up to 60 ppm in 0.05% N steels shows remarkably lower creep rupture strength. After controlled heat treatment, in which the tempering temperature is lower, such effect of high N content on creep strength was not observed but increasing the B content in high N steel does not show an increase in the creep strength: almost the same rupture life is obtained for Steels B1 (0.05 N, 10 ppm B) and Steel B2 (0.05 N, 60 ppm B). On the other hand, increasing the B content in 0.02% N steels shows higher creep strengths for both as-received and controlled heat-treated conditions.

(2) No other precipitates rather than $M_23C_6$ and Fe$_2$W were detected by EDS analysis and these precipitates occur along prior austenite grain boundary and inside the grain. TEM revealed that the stability of the matrix against recovery reaches maximum in the low N steels, while this stability is very weak in the high N–high B steel.

(3) ATE micrographs of tempered and crept specimens showed that the number density of precipitates containing B was highest in the high N–high B steel of which creep strength was lowest. ATE also indicated that much more free B existed in the matrix of the low N–high B steel of which creep strength is highest. Therefore, free B in solid solution is more effective on stabilization of microstructure and strengthening than B contained in precipitates, namely $M_23C_6$ carbides.

(4) Boron in steels of a suitable content of N is contributable to enhancement of creep strength through increasing the amount and the stability of fine precipitates such as VN, and dislocation microstructure. High content of N is expected to reduce such effects of B probably through the precipitation of BN, although no experimental evidence has been obtained.

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REFERENCES