DEVELOPMENT OF CREEP RESISTANT 9Cr-3W-3Co STEEL CONTAINING HIGH BORON FOR USC BOILERS

Hiroyuki Semba and Fujio Abe
National Research Institute for Materials Science (NIMS),
1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

ABSTRACT

In the R&D project of NIMS for advanced ferritic heat resistant steels for 650°C-USC plants, it has been revealed that the addition of boron more than 0.01mass% to the 0.08C-9Cr-3W-3Co-VNb-<0.003N steel remarkably improves long-term creep strength. The boron enriched in $M_{23}C_6$ carbides near prior-austenite grain boundaries suppresses coarsening of these carbides during creep deformation, leading to excellent microstructural stability and creep strength. Further improvement of creep strength is achieved by the addition of appropriate amount of nitrogen which enhances precipitation of fine MX. Excess addition of nitrogen to the high-boron containing steel reduces creep rupture lives and ductility. This degradation of creep strength is due to a decrease in the amount of effective boron, which is dissolved in $M_{23}C_6$ and suppresses its coarsening, resulting from the formation of coarse BN at normalizing temperature. The highest creep strength is obtained with the 0.08C-9Cr-3W-3Co-0.2V-0.05Nb-0.008N-0.014B (mass%) steel, resulting in excellent creep strength in comparison with that of P92. The 10^5 hours extrapolated creep rupture strength at 650°C is about 100MPa. This steel also shows good creep ductility even in the long term. It is, therefore, concluded that this high-boron bearing 9Cr-3W-3Co-VNb steel with the addition of nitrogen in the order of 0.008mass% is the promising candidate which shows superior creep strength without impairing creep ductility for thick section components in the 650°C-USC plants.

KEYWORDS

9Cr steel, creep, martensite, microstructural stability, $M_{23}C_6$, MX, boron, nitrogen, BN

INTRODUCTION

It is required to improve the efficiency of fossil-fired power plants in order to reduce the CO_2 emission. Therefore, development of ultra-super critical (USC) power plant aiming for steam temperatures of 650-750°C has been forwarded in Japan, USA and EU countries. Successful development of new advanced heat resistant steels and alloys which can be applied at those temperatures, especially for thick section components is a key to attain this advanced USC plant. Many research and development projects on advanced USC steels were launched in recent years [1-4]. Austenitic steels are advantageous in terms of high temperature strength; however, ferritic steels having tempered martensitic microstructure are favourable for thick sections in boilers such as main steam pipes in terms of thermal fatigue resistance. Hence, development of new ferritic heat resistant steels having excellent creep strength is the most important issues.

Tempered martensitic 9-12%Cr steels bearing tungsten, such as P92 and P122 showing higher creep rupture strength than the conventional steel P91, have been developed for thick section components in USC boilers [5]. However, their creep strength is not sufficient for applying at 650°C and above. Since 1997, NIMS has carried out the research and development on advanced ferritic heat resistant steels which can be applied at 650°C/35MPa as boiler components with large diameter and thick section [6]. In this project, it has been revealed that the addition of boron more than 0.01mass% to the 0.08C-9Cr-3W-3Co-VNb steel remarkably improves long-term creep strength [7-9], resulting in excellent creep strength in comparison with that of P92. It has also been demonstrated that Type IV failure does not occur during creep tests at 650°C performed on welded joints of these high-boron containing steels even at the stresses in which P92 shows Type IV fracture [10]. In this paper, alloy design and creep properties of the developed steel are described.

1. ALLOY DESIGN

1.1. SUPPRESSING DEGRADATION OF LONG-TERM CREEP STRENGTH BY ADDITION OF BORON

Drastic degradation of long-term creep rupture strength in 9-12%Cr ferritic heat resistant steels is a crucial problem. It has been revealed that inhomogeneous recovery of lath martensitic microstructure in the vicinity of prior austenite grain boundaries causes a sudden decrease in long-term creep rupture lives [11]. The authors have tried to stabilize the martensitic microstructure by the addition of large amount of boron more than 0.01mass%. Table 1 shows the chemical compositions of the steels examined in order to clarify the effect of boron. 0.08C-9Cr-3W-3Co-0.2V-0.05Nb (mass%) is the base composition of the steels. The boron content is changed from 0 to 0.0139 (mass%). No nitrogen was added in order to avoid the formation of coarse boron nitrides. The resultant nitrogen content is less than 0.0034mass%. Normalizing was carried out at 1050°C (the 0B, 0.0048B and 0.0092B steels) and 1080°C (the 0.0139B steel) for 1 hour, followed by tempering at 790°C (the 0B, 0.0048B and 0.0092B steels) and 800°C (the 0.0139B steel) for 1 hour.

Table 1. Chemical compositions of the steels tested (mass%).

	C	Si	Mn	Cr	W	Co	V	Nb	N	B
0B	0.078	0.31	0.50	8.94	2.94	3.03	0.19	0.050	0.0019	<0.0001
0.0048B	0.077	0.29	0.51	8.95	2.93	3.03	0.19	0.050	0.0011	0.0048
0.0092B	0.075	0.29	0.50	8.96	2.92	3.01	0.19	0.049	0.0016	0.0092
0.0139B (0.0034N)	0.078	0.30	0.51	8.99	2.91	3.01	0.19	0.050	0.0034	0.0139

Fig.1 shows creep rupture strength of the 0B, 0.0048B, 0.0092B and 0.0139B steels at 650°C. It is noted that the 0.0139B steel shows the highest and stable long-term creep rupture strength. It is about one order of magnitude longer than that of the P92 steel [12], which is the current advanced ferritic heat resistant steel. It also shows excellent rupture ductility even in the long term. Reduction of area for the crept specimen ruptured at more than 10000h is about 69-75%, in which P92 shows insufficient ductility of less than 50%. This superior ductility of the high-boron bearing steel also leads to good creep-fatigue resistance [13]. Although there is no substantial difference between the 0B, 0.0048B and 0.0092B steels at higher stresses than 100MPa, only the 0.0139B steel exhibits longer rupture time. This may be related with the difference in the amount of dissolved nitrogen. At lower stresses than 100MPa, the 0.0139B steel still shows stable creep rupture strength, while time to rupture in the lower boron bearing steels remarkably falls down with decreasing boron content. These results indicate that boron mainly suppresses the degradation in the long-term creep rupture strength of 9Cr-3W-3Co-VNb steels.

HOME

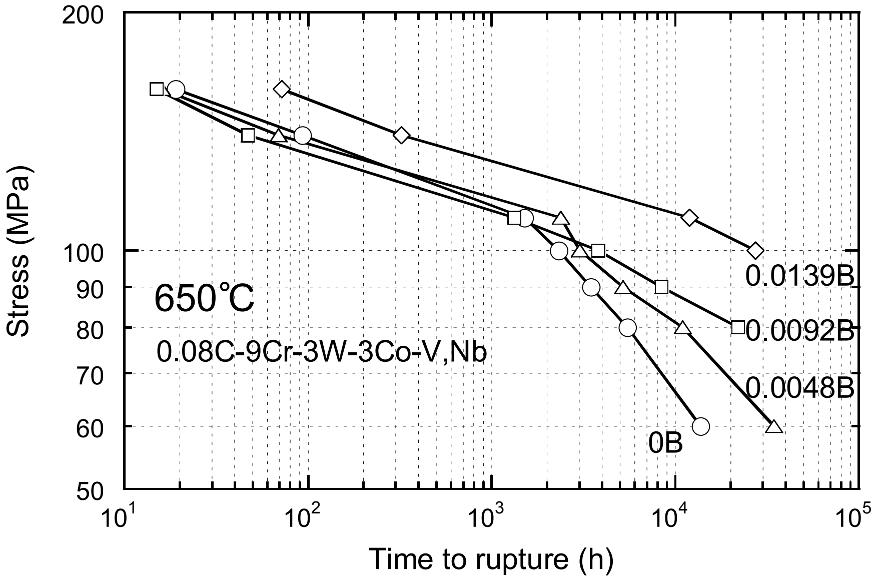

Fig. 1. Creep rupture strength of the various boron-containing 9C-3W-3Co-VNb steels at 650°C.

Fig. 2 shows the creep rate versus time curves of these boron containing steels at 80MPa. There is no major difference in creep rates through the primary creep region except the 0.0139B steel. The creep rate of the 0.0139B steel is lower than other steels in the primary region. It is noted that the addition of boron retards the onset time of tertiary creep, resulting in the lowest minimum creep rate and the longest time to rupture in the 0.0139B steel. It is also demonstrated that minimum creep rate of the 0.0139B steel is lower than that of the 0B and lower boron containing steels by almost one to two orders of magnitude. Similar results are obtained at higher stresses. Azuma *et al.* [14] have reported that boron does not affect Ac_1, Ac_3, Ms and M_f temperatures in the 0.1C-10.2Cr-0.7Mo-1.8W-3Co-VNbN steel. This designates that there is little difference in initial lath width and dislocation density, which can be affected by transformation temperature, in spite of the boron content. Fig. 3 shows the chemical analysis results of extracted residues in as tempered steels. It can be seen that about 90% of added boron is contained in precipitates after tempering.

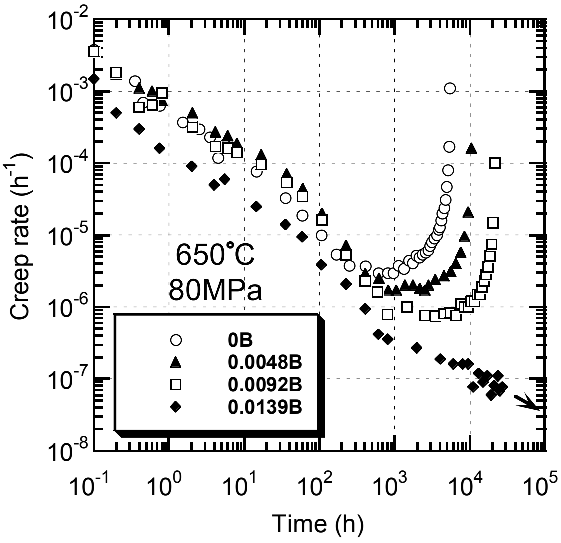

Fig. 2. Creep rate vs. time curves of 9Cr-3W-3Co -V,Nb steels.

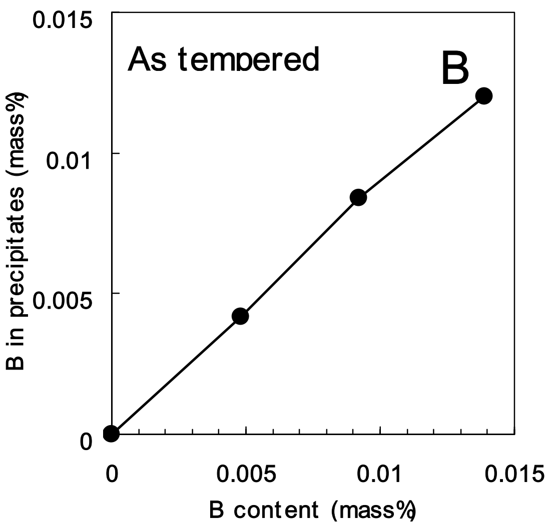

Fig. 3. Chemical analysis results of extracted residues in as tempered steels.

HOME

In order to reveal the effect of boron on the stability of carbides, mean diameter of $M_{23}C_6$ is measured by image analysis of FE-SEM micrographs for the as tempered and aged steels. Fig. 4 shows the measurement results of the 0B and 0.0139B steels. The area of 'near prior austenite grain boundaries (PAGB)' is defined as that within 10μm from PAGB. There is no difference in the mean diameter of $M_{23}C_6$ in the near PAGB and center of prior austenite grain (PAG) areas between the 0B and 0.0139B steels. However, coarsening of $M_{23}C_6$ on PAGB after long-term aging is drastically suppressed in the 0.0139B steel. Fig. 5 shows mean diameters of $M_{23}C_6$ on PAGB in the 0B, 0.0048B, 0.0092B and 0.0139B steels. Coarsening of $M_{23}C_6$ on PAGB after aging for 10300h is suppressed with increasing boron content. This corresponds to the trend of suppressing the degradation of creep rupture strength at around 10000h. As mentioned above, almost 90% of added boron precipitates after tempering. This precipitated boron may mainly exist as $M_{23}(C,B)_6$. Boron concentration in $M_{23}C_6$ in the 0.0139B steel after aging for 10300h has been analyzed by field emission scanning Auger spectroscopy (FE-AES). It has been revealed that boron is enriched in the $M_{23}C_6$ on the prior austenite grain boundaries and in its vicinity (within 5μm) [7]. Therefore, this may suppress the coarsening of $M_{23}C_6$ on the grain boundaries during creep deformation, resulting in the excellent creep rupture strength in the 0.0139B steel through stabilizing lath martensitic microstructures and preventing inhomogeneous deformation in the vicinity of PAGB.

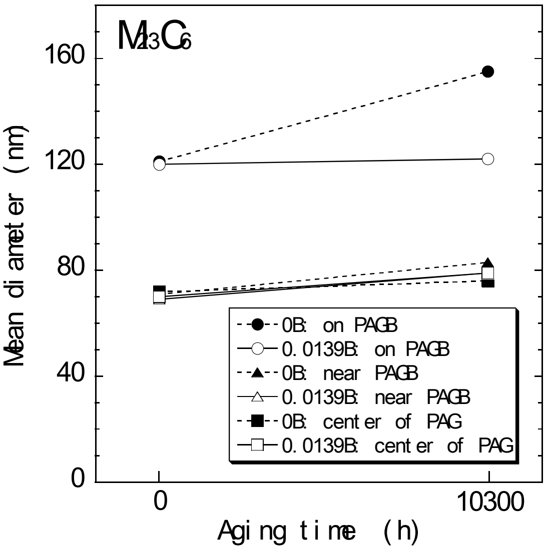

Fig. 4. Effect of boron on mean diameter of $M_{23}C_6$ in the 0B and 0.0139B steels. (PAGB: Prior austenite grain boundaries)

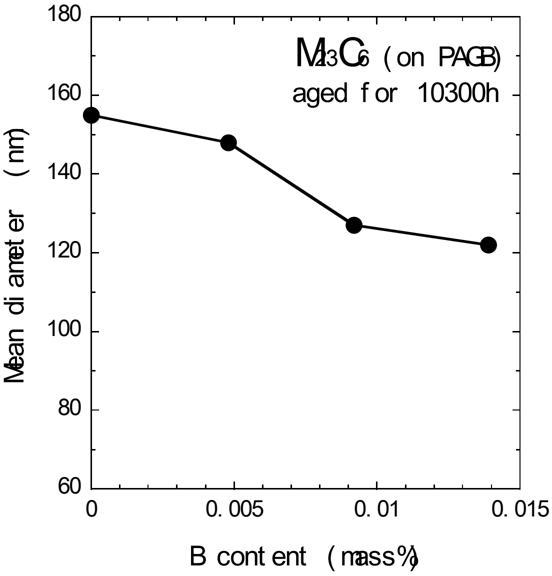

Fig. 5. Effect of boron content on mean diameter of $M_{23}C_6$ on prior austenite grain boundaries.

1.2. IMPROVEMENT OF CREEP STRENGTH BY ADDITION OF NITROGEN

The 0.08C-9Cr-3W-3Co-0.2V-0.05Nb (mass%) steel containing more than 0.01mass% boron shows very high and stable creep rupture strength at 650°C. However, further improvement of creep strength is required in order to achieve the target 10^5 hours rupture strength of 100MPa at 650°C. The results mentioned above also suggest that small amount of nitrogen affects creep strength of these steels. Therefore, the effect of nitrogen content on creep strength was investigated for 0.08C-9Cr-3W-3Co-0.2V-0.05Nb-0.014B steels. Table 2 shows the chemical compositions of the steels tested. The nitrogen content is changed from 0.0015 to 0.065 (mass%). Normalizing was carried out at 1150°C for 1 hour, followed by tempering at 770°C for 4 hours.

Table 2. Chemical compositions of the steels tested (mass%).

	C	Si	Mn	Cr	W	Co	V	Nb	N	B
0.0015N	0.076	0.30	0.51	9.00	3.02	3.02	0.19	0.053	0.0015	0.0132
0.0079N	0.078	0.31	0.49	8.88	2.85	3.00	0.20	0.051	0.0079	0.0135
0.065N	0.081	0.31	0.51	8.90	3.07	3.00	0.20	0.054	0.065	0.0144

Fig. 6 shows creep rupture strength of these steels containing nitrogen from 0.0015 to 0.065 (mass%). The 0.0034N steel is the same one as the 0.0139B steel shown in Fig. 1. It is noted that creep rupture strength remarkably increases with increasing nitrogen content from 0.0015 to 0.0079 (mass%). The 10^5 hours extrapolated rupture strength of 100MPa at 650°C, which is the target strength, can be accomplished by the 0.0079N steel. However, excess addition of nitrogen in the order of 0.065mass% reduces creep rupture strength. That of the 0.065N steel is lower than the 0.0079N steel in the short term and suddenly falls down in the long term more than 4000h. Minimum creep rate of these steels at 650°C and 120MPa is exhibited in Fig. 7. It decreases with increasing nitrogen content and the lowest creep rate is obtained with the 0.0079N steel. Further addition of nitrogen increases minimum creep rate. It is, therefore, concluded that the highest creep strength of this 0.014mass% boron bearing steel is obtained by the addition of around 0.008mass% nitrogen. Creep rate versus time curves of these 9Cr-3W-3Co-0.2V-0.05Nb-0.014B (mass%) steels at 650°C and 120MPa are shown in Fig. 8. The addition of nitrogen drastically decreases creep rate in the primary region and minimum creep rate by almost two orders of magnitude. The resultant onset time of tertiary creep is significantly retarded and creep rupture lives increase by one to two orders of magnitude. There is no difference in the creep rate of the primary region between the 0.0079N and 0.065N steels. However, the onset time of tertiary creep in the 0.065N steel is earlier than that in the 0.0079N steel, resulting in shorter time to rupture.

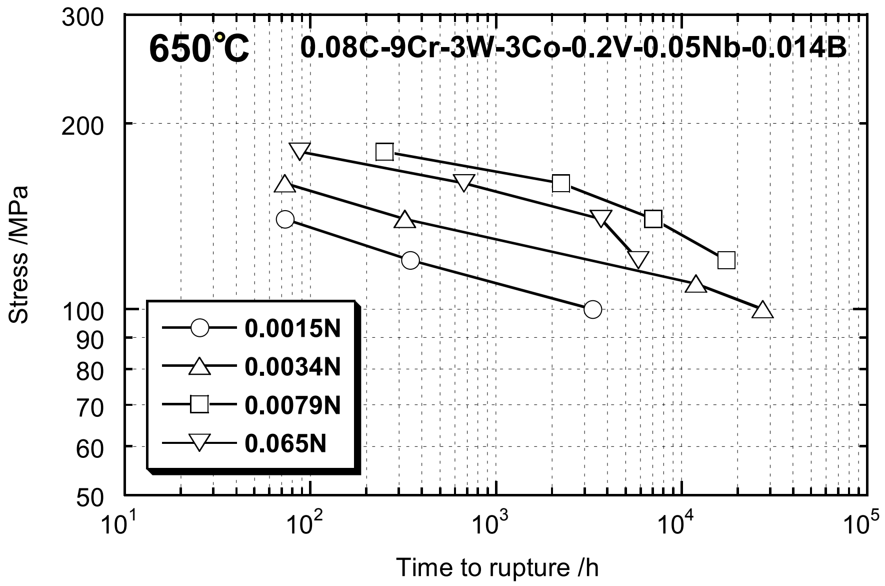

Fig. 6. Creep rupture strength of 9Cr-3W-3Co-VNb-0.014B steels containing 0.0015-0.065 (mass%) nitrogen at 650°C.

HOME

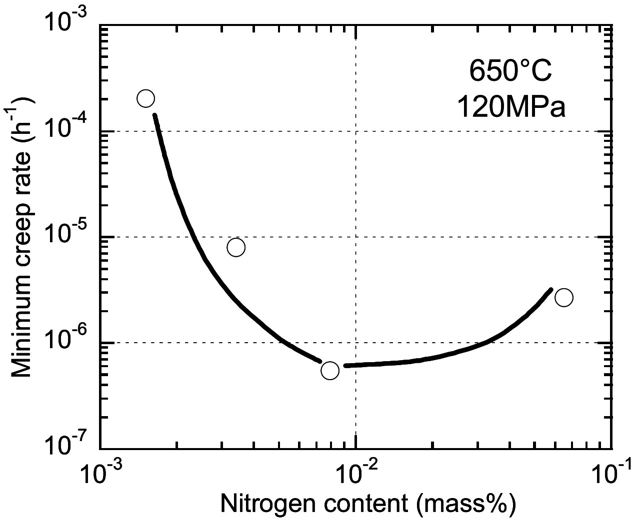

Fig. 7. Minimum creep rate of 9Cr-3W-3Co-VNb-0.014B steels containing 0.0015-0.065 (mass%) nitrogen at 650°C and 120MPa.

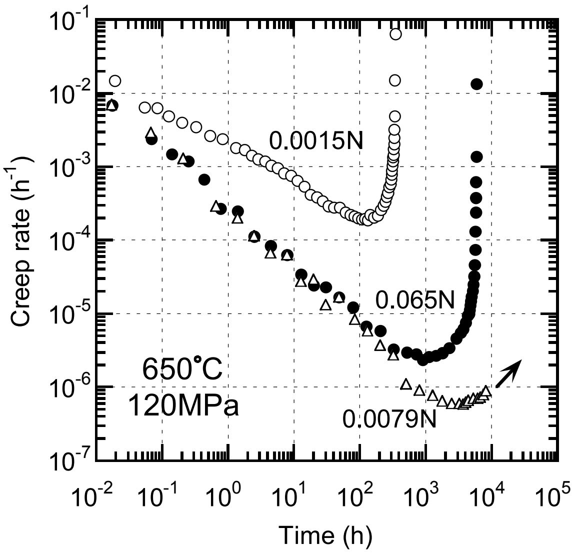

Fig. 8. Creep rate vs. time curves of 9Cr-3W-3Co -VNb-0.014B steels.

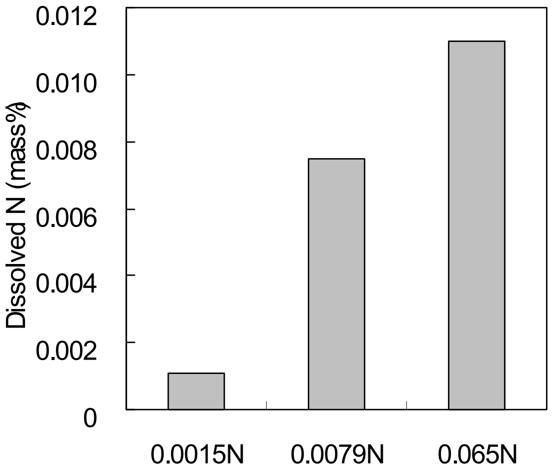

Fig. 9. Dissolved N in as tempered steels.

Chemical analysis of extracted residues was carried out for as tempered steels in order to clarify the effect of nitrogen on precipitation behavior. Fig. 9 shows the amount of dissolved nitrogen calculated from the amount of extracted residues and the total amount of nitrogen. Those of the 0.0079N and 0.065N steels are much higher than the 0.0015N steel. This result indicates that more MX precipitates in the 0.0079N and 0.065N steels during creep at 650°C and contributes to creep strength. Indeed, very fine V-rich MX was confirmed in the 0.0079N steel aged at 650°C for 1000h by TEM observation of extracted replica (Fig. 10). These fine precipitates of MX in the higher nitrogen containing steels drastically decrease creep rate in the transient creep region, resulting in lower minimum creep rate than the 0.0015N steel by almost two orders of magnitude. However, excess addition of nitrogen in the order of 0.065mass% decreases creep rupture strength as shown in Figs. 6 and 8. Coarse BN is observed in the as tempered 0.065N steel (Fig. 11). This is consistent with the observation results of BN in high-Cr steels at normalizing temperatures

HOME

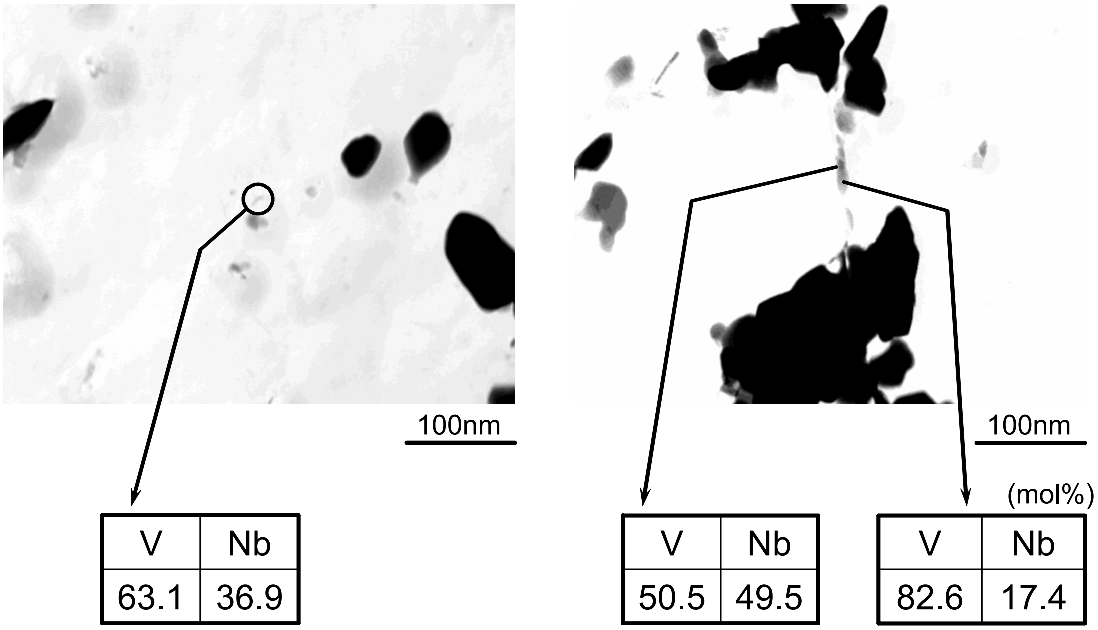

Fig. 10. TEM micrographs of the extracted replica for the 0.0079N steel aged at 650°C for 1000h.

by Sakuraya *et al* [15]. They have reported the solubility product for boron nitrides as follows:

$$\log [\%B] = -2.45 \log [\%N] - 6.81 \tag{1}$$

where [%B] and [%N] are concentration of boron and nitrogen in mass% respectively. Solution limit of nitrogen is obtained with equation (1) as 0.0095mass% for 0.014mass% boron. Hence, all the added boron in the 0.0079N steel can be dissolved in the matrix or $M_{23}C_6$ without formation of coarse BN at the normalizing temperature. On the other hand, most of the added boron may be consumed as coarse BN in the 0.065N steel. Therefore, the amount of effective boron, which is dissolved in $M_{23}C_6$ and suppresses its coarsening, in the 0.065N steel may be less than that in the lower nitrogen containing steels. Table 3 shows the equilibrium composition of $M_{23}C_6$ at 650°C calculated with Thermo-Calc considering the formation of BN. It is noted that the dissolved boron within $M_{23}C_6$ in the 0.065N steel is less than that in the 0.0015N and 0.0079N steels. This supports the above estimation and indicates that the amount of effective boron in the 0.065N steel is less than the 0.0015N and 0.0079N steels. The difference in the amount of effective boron may lead to large coarsening rate of $M_{23}C_6$ in the 0.065N steel, resulting in advancing onset time of acceleration creep and reducing time to rupture.

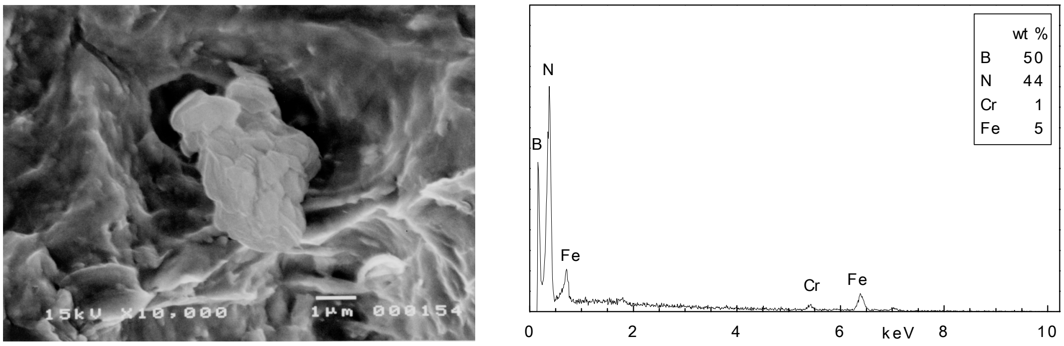

Fig. 11. BN observed in the as tempered 0.065N steel.

HOME

Table 3　Equilibrium compositions of $M_{23}C_6$ computed by Thermo-Calc (650°C).

(mol%)

	Cr	Fe	Mn	W	V	Co	C	B
0.0015N	64.88	12.26	1.39	0.32	0.33	0.12	15.59	5.11
0.0079N	64.89	12.15	1.41	0.36	0.38	0.11	15.99	4.71
0.065N	64.03	12.20	1.72	1.10	0.15	0.11	18.45	2.24

Chemical composition of the matrix:
0.08C-0.3Si-0.5Mn-9Cr-3W-3Co-0.2V-0.05Nb-0.0135B (mass%)

2. MICROSTRUCTURE AND CREEP PROPERTIES OF DEVELOPED STEEL

The nominal composition of the developed steel is 0.08C-0.3Si-0.5Mn-9Cr-3W-3Co-0.2V-0.05Nb-0.008N-0.014B (mass%). Plates of the developed steel were produced from a 180kg-ingot by hot forging and employed for creep tests. Microstructures of the developed steel after normalizing at 1150°C for 1 hour, followed by tempering at 770°C for 4 hours are shown in Fig. 12. The developed steel has a single phase microstructure of tempered martensite. No δ-ferrite was observed. Transformation temperatures are shown in Table 4.

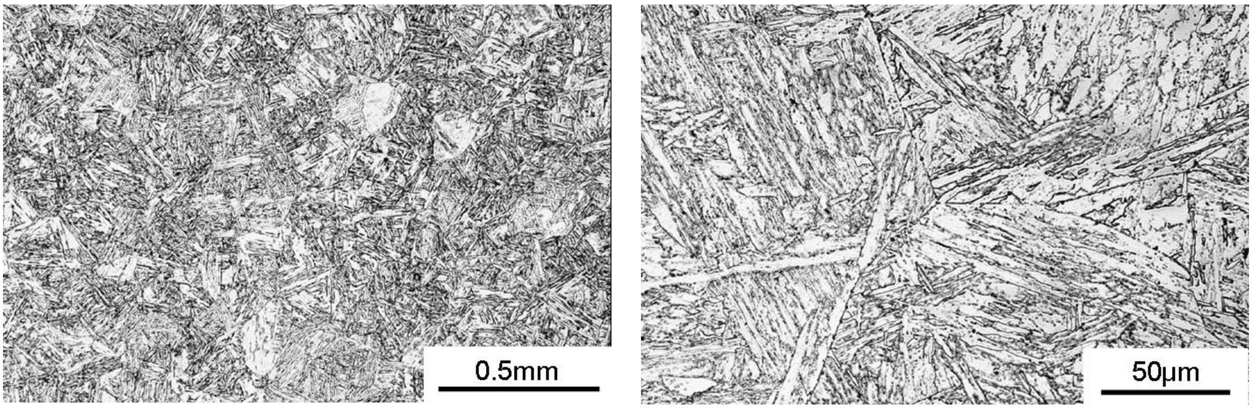

Fig. 12.　Optical micrographs of the developed steel (as tempered).

Table 4　Transformation temperatures of the developed steel (°C).

Ac1	Ac3	Ms	Mf
818	902	445	238

Fig. 13 shows creep rupture strength of the developed steel at 650°C compared with that of P92 [10] and T91 [16]. This developed steel shows stable long-term creep strength. Its rupture strength is more than one order of magnitude longer than that of the P92 steel. The 10^5 hours extrapolated rupture strength of 100MPa may be accomplished by the developed steel. Elongation and reduction of area after creep tests are shown in Figs. 14 and 15. It is noted that the developed steel has good creep ductility even in the long term especially compared with P92. It has been revealed that excess addition of nitrogen to these high-boron bearing steels reduces creep ductility [17]. Formation of coarse BN is considered to be responsible for a decrease in the creep ductility. Excellent creep strength and sufficient creep ductility are accomplished by the optimized balance of boron and nitrogen content as mentioned in the previous section.

HOME

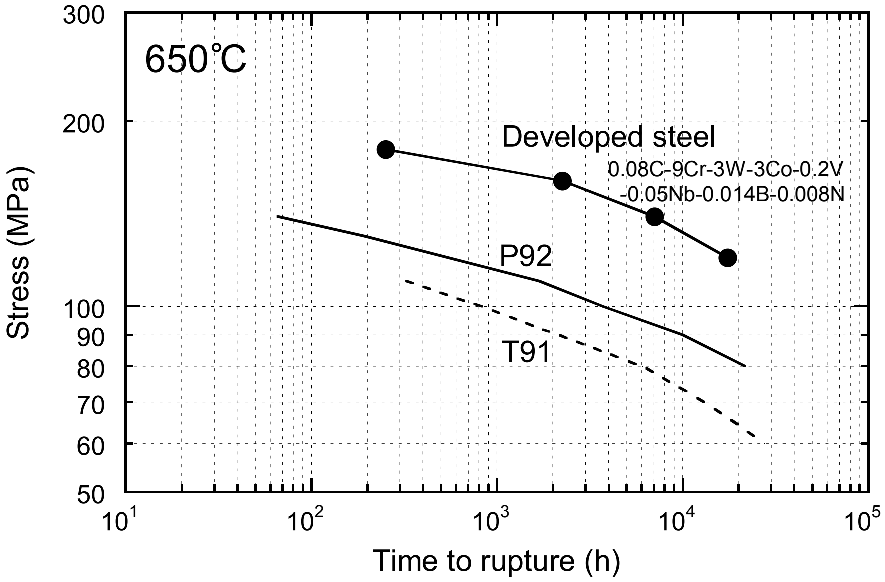

Fig. 13. Creep rupture strength of the developed steel.

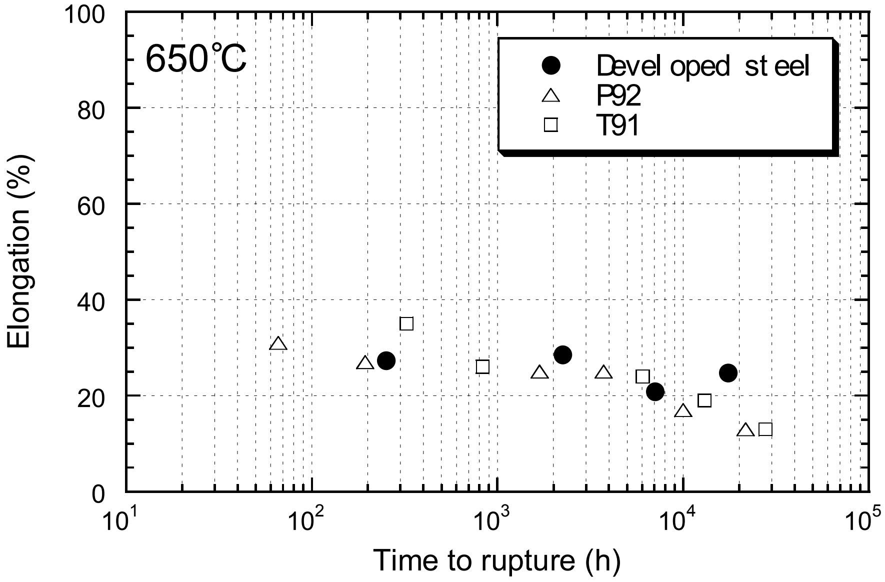

Fig. 14. Creep rupture ductility of the developed steel (Elongation).

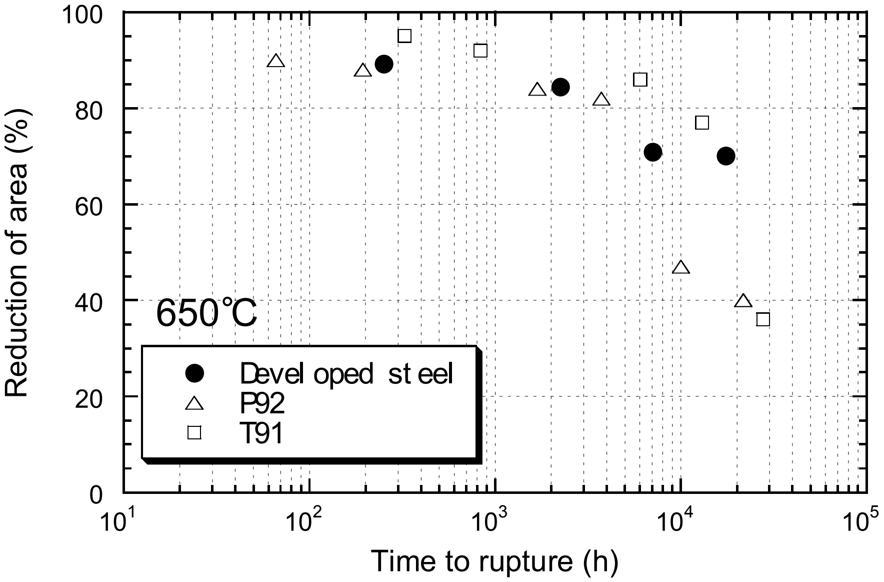

Fig. 15. Creep rupture ductility of the developed steel (Reduction of area).

3. CONCLUSIONS

The addition of boron more than 0.01mass% to 0.08C-9Cr-3W-3Co-0.2V-0.05Nb steel remarkably improves long-term creep strength. It retards the onset time of tertiary creep, resulting in increasing time to rupture. Boron stabilizes the lath martensitic microstructure of 9Cr-3W-3Co steels during creep deformation at 650°C through the stabilization of $M_{23}C_6$ in the vicinity of prior austenite grain boundaries by an enrichment of boron in the $M_{23}C_6$ carbides. Further improvement of creep rupture strength in this high-boron containing steel is accomplished by the addition of appropriate amount of nitrogen enhancing precipitation of fine MX. The highest creep strength is obtained with the 0.08C-9Cr-3W-3Co-0.2V-0.05Nb-0.008N-0.014B (mass%) steel, resulting in excellent creep strength in comparison with that of P92. This steel shows good creep-rupture ductility even in the long term. Hence, it is concluded that this developed steel is the promising candidate which shows superior creep strength without impairing creep ductility for thick section components in 650°C-USC plants.

ACKNOWLEDGEMENT

The creep tests were performed by the Creep Group in Materials Information Technology Station, NIMS. The authors are grateful to member of the Creep Group for their sincere efforts.

REFERENCES

1) R. Viswanathan, J.F. Henry, J. Tanzosh, G. Stanko, J. Shingledecker and B. Vitalis: Proceedings of the 4th International Conference on Advances in Materials Technology for Fossil Power Plants (CD-ROM), 2004, Hilton Head Island (USA), p.3

2) F. Masuyama: Proceedings of the 4th International Conference on Advances in Materials Technology for Fossil Power Plants (CD-ROM), 2004, Hilton Head Island (USA), p.35.

3) B. Scarlin, M. Staubli and T.U. Kern: Proceedings of the 4th International Conference on Advances in Materials Technology for Fossil Power Plants (CD-ROM), 2004, Hilton Head Island (USA), p.81.
4) R. Blum, R.W. Vanstone and C. Messelier-Gouze: Proceedings of the 4th International Conference on Advances in Materials Technology for Fossil Power Plants (CD-ROM), 2004, Hilton Head Island (USA), p.118.
5) F. Masuyama: Advanced Heat Resistant Steels for Power Generation, R. Viswanathan and J. Nutting (eds.), The Institute of Materials, London, 1998, p.33.
6) F. Abe, M. Tabuchi, K. Sawada, S. Kuroda, H. Okada and S. Muneki: Proceedings of the second International Conference on Advanced Structural Steels, 2004, The Chinese Society for Metals, p.757.
7) T. Horiuchi, M. Igarashi and F. Abe: ISIJ International, 42(2002), Supplement, p.S67.
8) K. Sawada, T. Horiuchi, K. Kimura and F. Abe: Current Advances in Materials and Processes, Report of the ISIJ Meeting, 15(2002), p.1248.
9) F. Abe, T. Horiuchi, M. Taneike and K. Sawada: Mat. Sci. Eng. A, 378(2004), p.299.
10) M. Kondo, M. Tabuchi, S. Tsukamoto, F. Yin and F. Abe: Proceedings of the second International Conference on Advanced Structural Steels, 2004, The Chinese Society for Metals, p.834.
11) K. Kimura, H. Kushima and F. Abe: Key Engineering Materials, 171-174(2000), p.483.
12) NIMS Creep Data Sheet No.48, National Institute for Materials Science, Tsukuba, (2002)
13) M. Kimura, K. Kobayashi and K. Yamaguchi: Mat. Sci. Res. Int., 9(2003), p.50.
14) T. Azuma, K. Miki, Y. Tanaka and T. Ishiguro: Tetsu-to-Hagané, 89(2003), p.349.
15) K. Sakuraya, H. Okada and F. Abe: Proceedings of the Second International Conference on Advanced Structural Steels, 2004, The Chinese Society for Metals, p.772.
16) NIMS Creep Data Sheet No.43, National Institute for Materials Science, Tsukuba, (1996)
17) H. Semba and F. Abe: Proceedings of the 4th International Conference on Advances in Materials Technology for Fossil Power Plants (CD-ROM), 2004, Hilton Head Island (USA), p.1254.

HOME