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Effect of Boron on Microstructure and Creep Strength of Advanced Ferritic Power Plant Steels

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Abstract

The boundary and sub-boundary hardening is shown to be the most important strengthening mechanism in creep of 9Cr steel. The soluble boron reduces the coarsening rate of $M_{23}C_6$ carbides along boundaries near prior austenite grain boundaries during creep, enhancing the boundary and sub-boundary hardening for up to long times. The enhancement of boundary and sub-boundary hardening retards the onset of acceleration creep, which decreases the minimum creep rate and improves the creep life. Excess addition of boron and nitrogen promotes the formation of boron nitrides during normalizing heat treatment, which significantly reduces soluble boron and nitrogen concentrations and offsets the benefit due to boron and nitrogen.

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1. Introduction

The materials developments for advanced steam conditions of 700 °C have already been initiated to achieve a net efficiency of higher than 50% in Europe, in the US and in Japan. These projects involve the replacement of 9 to 12% Cr martensitic steels with nickel-base superalloys for the components subjected to the highest temperatures. However, nickel-base superalloys are expensive. To minimize the requirement of expensive nickel-base superalloys, 9 to 12% Cr martensitic steels can be used for the components subjected to the next highest temperatures of such very high temperature plants. Therefore, the development of 9 to 12% Cr martensitic steels is highly desirable for expanding the present temperature range of 610 ^{o}C in maximum up to 650 °C.

Fine MX carbonitrides are known to be very effective for strengthening of 9 % Cr steel [1]. The addition of boron also improves the creep strength of 9% Cr steel at 650°C [2]. It should be noted that boron is a strong nitride forming element and that boron nitrides can form in 9 to 12% Cr steels during heat treatment at high temperatures, which consumes soluble boron and nitrogen. The present paper describes key metallurgy for achieving additive creep-strengthening due to boron and MX carbonitrides for tempered martensitic 9% Cr steel at 650°C.

2. Experimental Procedure

The 9Cr-3W-3Co-0.2V-0.05Nb steels with different boron contents of 0, 48, 92 and 139 ppm were used to investigate the effect of boron on creep strength of 9Cr boron steel base metals. Nitrogen was not added to the steel o avoid the formation of boron nitride during normalizing heat treatment at high temperatures. The chemical

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compositions of this series are given in Table 1 [2]. The 9Cr-3W-3Co-0.2V-0.05Nb steels with 140 ppm boron but different nitrogen contents were used to investigate the effect of nitrogen on creep strength of 9Cr boron steel. The chemical compositions of this series are given in Table 2 [3].   The steels were basically prepared by vacuum induction melting to 50 kg ingots. Hot forging and hot rolling were performed to produce plates of 20 mm in thickness. Creep tests were carried out at 650°C for up to about 7×10^4 h under constant load condition, using specimens of 10 mm in gauge diameter and 50 mm in gauge length.

Table 1 Chemical compositions and heat treatment conditions of 9Cr-3W-3Co-VNb steel with different boron concentrations

	C	Si	Mn	Cr	W	V	Nb	Co	N	B	normalizing	tempering
0 ppm B	0.078	0.31	0.50	8.94	2.94	0.19	0.050	3.03	0.002	<0.0001	1050 °C x 1 h	790 °C x 1 h
48 ppm B	0.077	0.29	0.51	8.95	2.93	0.19	0.050	3.03	0.001	0.0048	1050 °C x 1 h	790 °C x 1 h
92 ppm B	0.075	0.29	0.50	8.96	2.92	0.19	0.049	3.01	0.002	0.0092	1050 °C x 1 h	790 °C x 1 h
139 ppm B	0.078	0.30	0.51	8.99	2.91	0.19	0.050	3.01	0.003	0.0139	1080 °C x 1 h	800 °C x 1 h

Table 2 Chemical compositions and heat treatment conditions of 9Cr-3W-3Co-VNb steels with 0.014% (140 ppm) boron but different nitrogen concentrations

	C	Si	Mn	Cr	W	Co	V	Nb	N	B	normalizing	tempering
0.0015N	0.076	0.30	0.51	9.00	3.02	3.02	0.19	0.053	0.0015	0.0132	1150°C x 1 h	770°C x 4 h
0.0034N	0.078	0.30	0.51	8.99	2.91	3.01	0.19	0.049	0.0034	0.0139	1080°C x 1 h	800°C x 1 h
0.0079N	0.078	0.31	0.49	8.88	2.85	3.00	0.20	0.051	0.0079	0.0135	1150°C x 1 h	770°C x 4 h
0.030N	0.078	0.30	0.51	9.08	3.05	3.03	0.20	0.055	0.0300	0.0150	1150°C x 1 h	770°C x 4 h
0.065N	0.081	0.31	0.51	8.90	3.07	3.00	0.20	0.054	0.0650	0.0144	1150°C x 1 h	770°C x 4 h

3. Experimental Results and Discussion

3.1 Effect of boron on creep strength and microstructure

The effect of boron on creep deformation behavior is shown in Fig. 1, where the creep rate curves of the steels at 650 °C and 80 MPa are shown. The creep rate curves consist of a primary or transient creep region, where the creep rate decreases with time, and a tertiary or acceleration creep region, where the creep rate increases with time after reaching a minimum. There is no substantial steady-state region, at which the creep rate is constant. The present author has revealed that for tempered martensitic 9% Cr steel, transient creep is basically a consequence of the movement and annihilation of high-density dislocations produced by martensitic transformation during cooling after normalizing, and that the acceleration creep is a consequence of the gradual loss of creep strength due to the microstructure recovery [4]. The migration of lath or block boundaries, causing the coarsening of the laths or blocks, is closely correlated with the onset of acceleration creep. In Fig.1(a), the initial creep rates are approximately the same among the steels containing different boron concentrations, except for the steel with 139 ppm boron, which exhibits a slightly lower creep rate. This is due to the slightly higher nitrogen concentration in the steel with 139
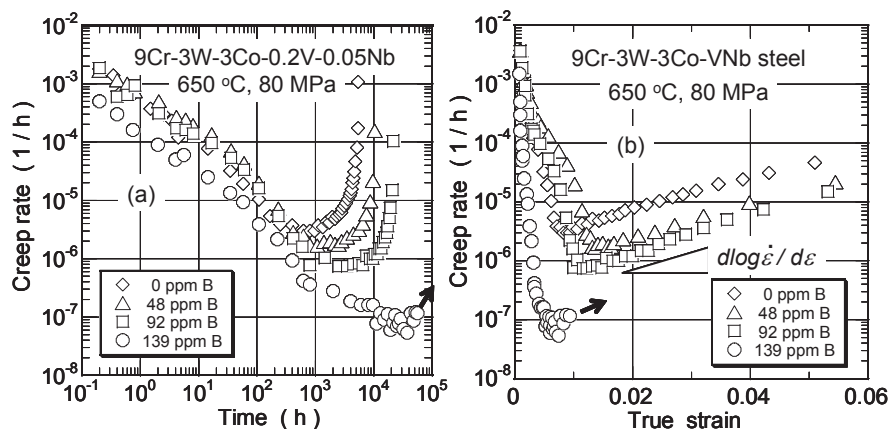

Fig. 1 Effect of boron on (a) creep rate versus time curves; (b) creep rate versus strain curves of the steels at 650 °C and 80 MPa

ppm boron. The onset of acceleration creep is retarded and the transient creep region continues for a longer time with increasing boron content. The longer duration of the transient creep region results in a lower minimum creep rate and a longer time to rupture. The addition of boron does not decrease the creep rate in the transient region, but it significantly decreases the minimum creep rate by retarding the onset of acceleration creep. The logarithmic creep rate increases linearly with strain for a wide range of strain in the acceleration creep region after reaching a minimum creep rate, Fig.1(b).   The value of $dln\,\dot{\varepsilon}\,/d\,\varepsilon$, which is equivalent to Omega parameter [5], is approximately the same among the different steels containing different boron content, although the addition of boron significantly decreases the minimum creep rate.

Only $M_{23}C_6$ carbides but no MX carbonitrides are distributed along the lath, block and packet boundaries and PAGBs after tempering. Analysis by scanning Auger spectroscopy for the steel with 139 ppm boron after aging at 650 °C for 10,300 h shows that boron is enriched in $M_{23}C_6$ carbides in the vicinity of the prior austenite grain boundaries (PAGBs) [2]. The enrichment of boron in $M_{23}C_6$ carbides is also observed after tempering, but it becomes more significant with increasing aging time. No evidence is found for the enrichment of boron in the Fe_2W Laves phase, which precipitated during creep at 650 °C. The fine distribution of $M_{23}C_6$ carbides along PAGBs is maintained in the steel with 139 ppm boron during exposure at elevated temperatures [6]. In the base steel without boron, a fine distribution of $M_{23}C_6$ carbides is observed after tempering but extensive coarsening takes place in the vicinity of PAGBs during creep. This indicates that the addition of boron reduces the rate of Ostwald ripening of $M_{23}C_6$ carbides in the vicinity of PAGBs during creep.

Fig. 2 shows the mechanism responsible for the improvement of time to rupture by the addition of boron. Because the $M_{23}C_6$ carbides are approximately the same size among the steels containing different boron concentrations after tempering, the steels have substantially the same creep rates in the initial creep stage. However, the high coarsening rate of $M_{23}C_6$ carbides in the vicinity of PAGBs promotes the migration of lath or block boundaries, and hence the onset of acceleration creep takes place earlier in the steels containing lower boron contents. The sub-boundary hardening enhanced by $M_{23}C_6$ carbides is the most important factor in long-term creep strengthening. Although the $M_{23}C_6$ carbides near PAGBs are much larger than those at the center of grains, the suppression of particle coarsening during creep and the maintenance of a homogeneous distribution of less fine $M_{23}C_6$ carbides near PAGBs are very effective for avoiding the degradation in creep strength and for improving long-term creep strength.
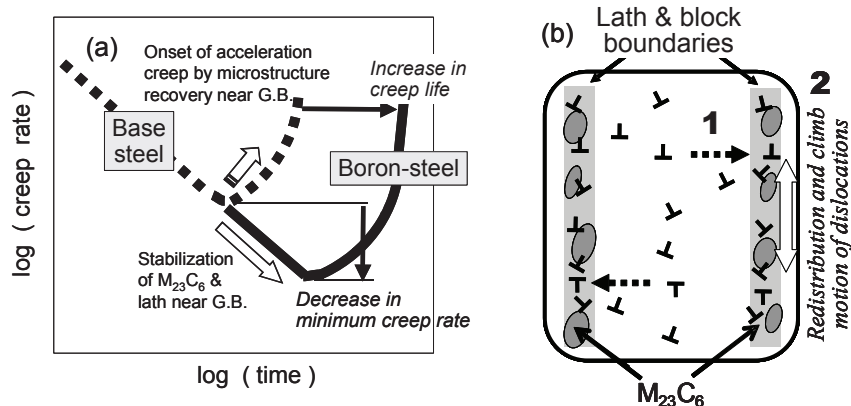

Fig. 2 Schematic illustrations showing (a) mechanism of effect of boron for improvement of time to rupture; (b) movement and annihilation of dislocations in the transient creep region

3.2 Combination of coarsening-resistant $M_{23}C_6$ carbides near PAGBs using boron and dispersion of fine MX carbonitrides

Soluble boron contributes to the enrichment in $M_{23}C_6$ carbides, and soluble nitrogen causes the precipitation of fine MX carbonitrides. Large boron nitride particles having a size of 1 μm or more have been sometimes observed in conventional 9 to 12% Cr steels after forging and after heat treatments at high temperatures, because boron is a strong nitride former. The formation of large boron nitride particles offsets the above benefits due to boron and nitrogen. The solubility product for boron nitride at 1050 to 1150 °C is given by [7]

$$log\ [\%B]\ =\ -2.45\ log\ [\%N]\ -\ 6.81, \qquad\qquad (1)$$

where [%B] and [%N] are the concentrations of soluble boron and soluble nitrogen in mass%, respectively. At a boron concentration of 140 ppm, only 95 ppm nitrogen can dissolve in the matrix without the formation of any boron nitride during normalizing.

Fig. 3 shows the effect of nitrogen addition on the creep rate versus time curves and creep rate versus strain curves, respectively, of the steel at 650°C and 120 MPa. The addition of nitrogen causes a rapid decrease in creep rate with time and also with strain in the transient region. It should be noted that the creep rate in the transient region is the same among the three steels containing different nitrogen of 79, 300 and 650 ppm. The onset of acceleration creep is retarded up to longer time by the addition of 79 ppm nitrogen but it shifts to earlier times with increasing nitrogen content above 79 ppm. The addition of small amount of nitrogen of 79 ppm to the steel with 140 ppm boron, which causes no formation of BN during normalizing, further decreases the creep rates in the transient region by precipitation strengthening due to fine MX and it also further retards the onset of acceleration creep, compared with those of 0.0015N steel. The onset of acceleration creep takes place at a high strain of 0.045 in the very low nitrogen 0.0015N steel as shown by the arrow, while it takes place at a low strain of 0.007 in the 0.0079N, 0.030N and 0.065N steels. This suggests that the addition of nitrogen promotes the heterogeneity in creep deformation.
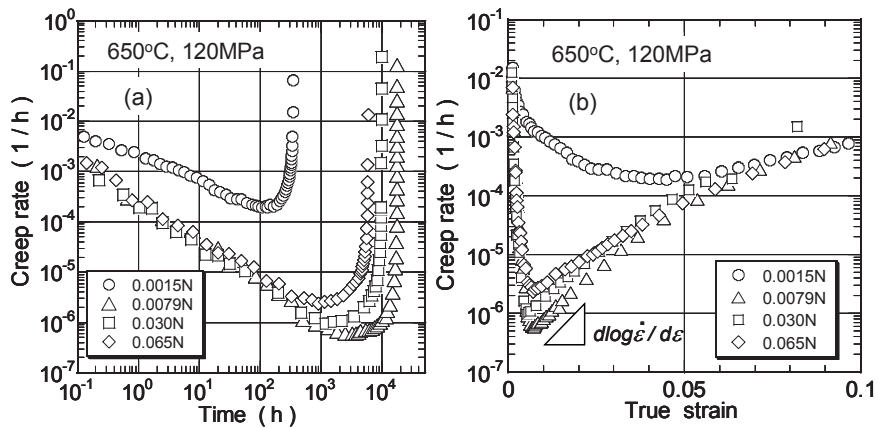

Fig. 3 Effect of nitrogen on creep rate versus time curves and creep rate versus strain curves of the steels at 650°C and 120 MPa

The nitrogen concentration dependence of the time to rupture and the minimum creep rate at 650 °C and 120 MPa is shown in Fig.4. The peak time to rupture and the minimum creep rate are located at about 80 to 100 ppm nitrogen, which corresponds to the maximum solid solubility of nitrogen in equilibrium with boron nitride in the steel with 140 ppm boron at a normalizing temperature of 1100 °C. This indicates that the addition of a small amount of nitrogen without the formation of any boron nitride during normalizing significantly improves the creep strength but the formation of boron nitrides during normalizing causes the degradation of creep strength.
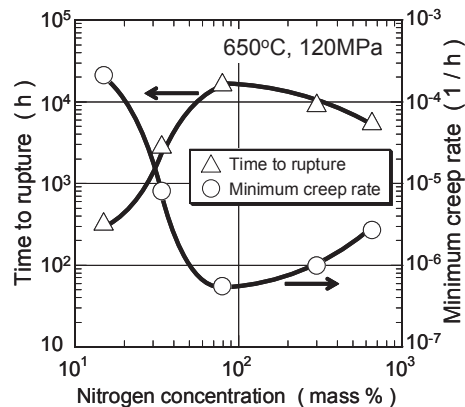

Fig. 4 Time to rupture and minimum creep rate of 9Cr-3W-3Co-0.2V-0.05Nb-0.08C steel with 140 ppm boron at 650 °C and 120 MPa as a function of nitrogen concentration

In the low nitrogen 0.0015N and 0.0079N steels, most of nitrogen is in solution after tempering. But in the high nitrogen 0.065N steel, most of nitrogen has already precipitated as MX carbonitrides during tempering. The dissolved nitrogen concentration is roughly the same between the 0.079N and 0.065N steels after tempering. Dissolved nitrogen can precipitate as fine MX carbonitrides during creep at 650°C. Indeed, very fine vanadium-rich MX carbonitrides were observed to have precipitated in the 0.0079N steel after aging for 1000 h at 650°C [3]. Fine MX carbonitrides precipitated during creep effectively decreases the creep rates in the transient region.

Fig. 5 compares the enrichment of boron in $M_{23}C_6$ carbides between the 0.0015N and 0.065N steels. In the 0.0015N steel, no boron nitride formed during normalizing heat treatment and hence most of boron can contribute to the enrichment in $M_{23}C_6$ carbides near PAGBs. On the other hand, in the 0.065N steel, large amount of boron nitrides formed during normalizing at high temperature. Therefore, most of boron is consumed to form the boron nitrides. This is a reason why the onset of acceleration creep takes place at earlier time in the high nitrogen steel. The present results suggest that a critical issue for the stabilization of martensitic microstructure is to increase soluble boron free from BN but not total boron content.
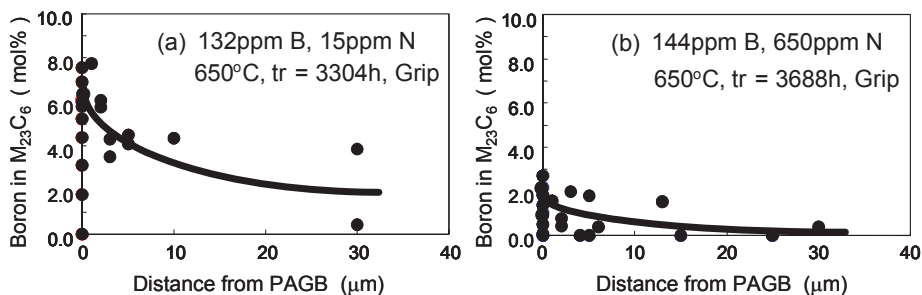

Fig. 5 Boron content in $M_{23}C_6$ carbides in the steels after creep rupture testing at 650°C for 3000-4000 h, as a function of distance from prior austenite grain boundary

Fig. 6 shows schematically the creep rate versus time curves of the 9Cr steel with various combinations of boron and nitrogen contents. Based on the base steel with no boron and no nitrogen, the addition of 140ppm boron but no addition of nitrogen, the curve 2 in Fig.6, retards the onset of acceleration creep, which effectively decreases the minimum creep rate and increases the creep life. The retardation is caused by the stabilization of martensitic microstructure near PAGBs by an enrichment of boron in $M_{23}C_6$ carbides. The addition of 140 ppm boron and small amount of nitrogen of 80 ppm, which causes no formation of BN during normalizing, decreases the creep rates in the transient region by precipitation strengthening due to fine MX and it also retards the onset of acceleration creep by the microstructure stabilization due to boron. However, the addition of 140 ppm boron and excess nitrogen of 650 ppm, which causes the formation of large amount of BN during normalizing, decreases the creep rates in the transient region similar as that in the steel with 80 ppm nitrogen but it promotes the onset of acceleration creep in comparison with the steel with 80 ppm nitrogen. The formation of large amount of BN during normalizing significantly reduces the dissolved boron concentration.
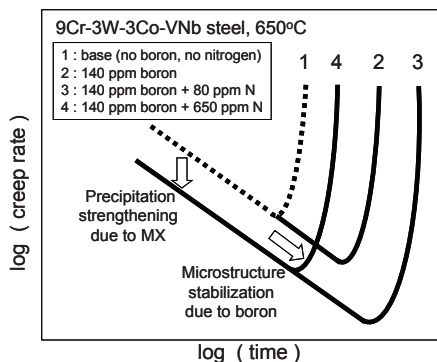

Fig. 6 Schematic creep rate versus time curves of the 9Cr-3W-3Co-VNb steel with various combinations of boron and nitrogen contents

   The grain boundary segregation of boron and the enrichment process of boron in $M_{23}C_6$ are shown in Fig.7. The grain boundary segregation of boron is estimated in the condition of no boron nitride formation. The initial boron concentration and the grain size are assumed to be 100 ppm and 50 μm, respectively. Using a binding energy of 62.7 kJ mol^{-1} [8] between grain boundary and boron reported for type 316 stainless steel, the segregation of several % boron can be achieved at grain boundaries at a normalizing temperature of 1100 °C. The formation of boron nitrides during normalizing heat treatment at high temperatures consumes most of boron added, which considerably reduces the grain boundary segregation of boron. This results in a significant decrease in enrichment of boron in $M_{23}C_6$ in the vicinity of PAGBs during tempering.
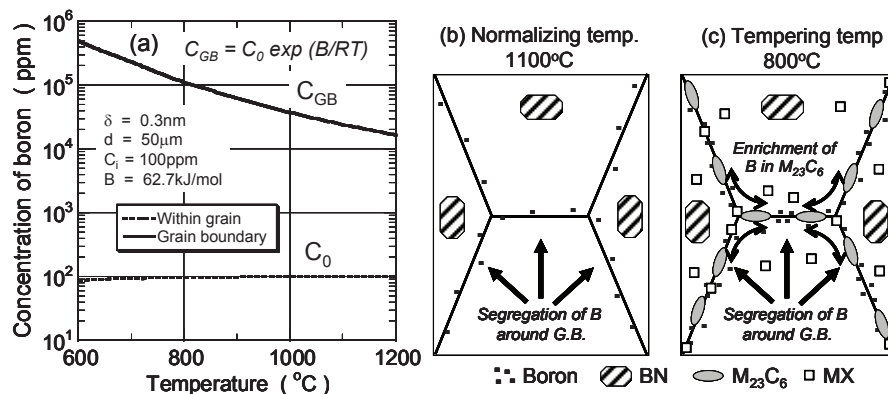

Fig. 7 (a) grain boundary segregation of boron; (b) and (c) formation process of $M_{23}(CB)_6$ during heat treatment

4. Conclusions

1) The addition of boron and nitrogen to 9Cr-3W-3Co-VNb steel without any formation of BN during normalizing at high temperature effectively decreases the creep rates in the transient region by precipitation strengthening due to fine MX and it also retards the onset of acceleration creep by microstructure stabilization due to boron. The addition of excess nitrogen of 300 and 650 ppm to the steel with 140 ppm boron causes the formation of large amount of BN during normalizing, which significantly reduces soluble boron available for microstructure stabilization.
2) The effect due to boron is to stabilize fine distribution of $M_{23}C_6$ carbides in the vicinity of PAGBs during creep.
3) It is concluded that the addition of boron and nitrogen without any formation of BN during normalizing heat treatment is essential to achieve additive strengthening due to boron and MX carbonitrides in 9Cr steel.

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