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TOPICAL REVIEW

Precipitate design for creep strengthening of 9% Cr tempered martensitic steel for ultra-supercritical power plants

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Received 26 September 2007
Accepted for publication 15 November 2007
Published 13 March 2008
Online at stacks.iop.org/STAM/9/013002

Abstract

It is crucial for the carbon concentration of 9% Cr steel to be reduced to a very low level, so as to promote the formation of MX nitrides rich in vanadium as very fine and thermally stable particles to enable prolonged periods of exposure at elevated temperatures and also to eliminate Cr-rich carbides \( M_23C_6 \). Sub-boundary hardening, which is inversely proportional to the width of laths and blocks, is shown to be the most important strengthening mechanism for creep and is enhanced by the fine dispersion of precipitates along boundaries. The suppression of particle coarsening during creep and the maintenance of a homogeneous distribution of \( M_23C_6 \) carbides near prior austenite grain boundaries, which precipitate during tempering and are less fine, are effective for preventing the long-term degradation of creep strength and for improving long-term creep strength. This can be achieved by the addition of boron. The steels considered in this paper exhibit higher creep strength at 650 °C than existing high-strength steels used for thick section boiler components.

Keywords: Ostwald ripening, \( M_23C_6 \) carbide, MX carbonitride, martensite, 9% Cr steel, creep strength, sub-boundary hardening

1. Introduction

Energy security combined with lower carbon dioxide emissions is increasingly considered necessary to protect the global environment in the 21st century. Coal provides us with abundant, low-cost resources for electric power generation. However, traditional coal-fired power plants emit large amounts of environmentally damaging gases such as CO\(_2\), NO\(_x\) and SO\(_x\) compared with other electric power generation methods. The adoption of ultra-supercritical (USC) power plants with increased steam parameters significantly improves efficiency, which reduces fuel consumption and the emissions of environmentally damaging gases. For example, the increase in steam parameters from the conventional 538/566 °C and 24.1 MPa to 650/593 °C and 34.3 MPa causes an increase in relative efficiency of 6.5%, which results in a significant decrease in coal use, and hence the reduction of CO\(_2\) emissions [1]. Power plants with steam parameters higher than the 538/566 °C and 24.1 MPa in conventional power plants are usually called USC plants. In Japan, part of coal-fired steam power plants has already been upgraded to the USC standards set in the 1990s, which are based on materials technology applying high-strength heat-resistant steels. This has enabled the steam temperature to be raised to about 600–610 °C. The increase in steam parameters at temperatures exceeding 600 °C requires the extensive research and development of advanced ferritic/martensitic steels with long-term creep rupture strength higher than that of conventional steels. The improvement of resistance to oxidation in high-temperature steam, resistance to type IV
cracking strength loss in welded joints [2] and also resistance to creep-fatigue damage are other issues.

Further advanced steam conditions of 700 °C and above have already been initiated to achieve a net efficiency of higher than 50% in the Thermie AD700 project in Europe [3], which has a target temperature of 700 °C and in the DOE Vision 21 project in the US [4], which initially aimed to achieve a steam temperature of 760 °C. These projects involve the replacement of 9–12% Cr martensitic steels with nickel-base superalloys for the components subjected to the highest temperatures. Nickel-base superalloys are much more expensive than ferritic/martensitic steels. To minimize the requirement of expensive nickel-base superalloys, 9–12% Cr martensitic steels can be used for components subjected to the next highest temperatures of such very high temperature plants. Therefore, the development of 9–12% Cr martensitic steels is highly desirable for expanding the present temperature range up to 650 °C and higher.

In this paper, we describe key issues in the precipitate design for the creep strengthening of tempered martensitic 9% Cr steel for thick section boiler components in USC plants at 650 °C.

2. Why tempered martensitic 9% Cr steel?

Ferritic steel has a body-centered cubic (bcc) crystal structure, but whether its microstructure is ferrite, bainite or martensite mainly depends on the concentration of alloying elements such as Cr and the heat treatment conditions. Figure 1 shows the effect of Cr concentration on the relationship between the ductile-to-brittle transition temperature (DBTT) after aging at 873 K (600 °C) for 1000 h and the creep rupture strength at 600 °C after 1000 h for (2–15)Cr-2W-0.1C steels [5]. In this figure, the line connecting the data points shows the effect of increasing Cr concentration. Vanadium, niobium and nitrogen were not added so that there were no MX carbonitride precipitates in the steels. For the increase in Cr from 2 to 5 to 9%, the range where the steels consist of tempered bainite or tempered martensite, the creep rupture strength increases markedly, but the DBTT increases only slightly. The microstructure evolution during creep, such as the recovery of excess dislocations and the coarsening of carbides and subgrains, is greater in the low-Cr bainitic steels than in the high-Cr martensitic steels. This reflects the smaller creep rupture strength of the bainitic 2Cr-2W steel than that of the martensitic 9Cr-2W steel. At high Cr concentrations above about 10%, where the steels consist of a dual phase of martensite and δ-ferrite, the creep rupture strength decreases and the DBTT increases with increasing Cr concentration, namely, with increasing volume fraction of δ-ferrite. The volume fraction of δ-ferrite increases with increasing Cr concentration: 0.16 and 0.60 for the 12Cr-2W and 15Cr-2W steels, respectively. The δ-ferrite contains no carbide, no subgrains and a fairly low density of dislocations. The lath, block and packet substructures in the tempered bainitic and martensitic microstructure are advantageous for toughness compared with the ferrite matrix of δ-ferrite. The optimum concentration of Cr from the point of view of creep strength and toughness is thought to be 9%. Recently, Miki et al [6] investigated the effect of Cr concentration on the time to rupture of 0.1C-0.2Ni-0.1Mo-0.15V-0.06Nb-3.5W-3Co-0.02N-0.01B steels containing 8.5, 9.0, 9.5, 10.0, 10.5 and 11.5% Cr for turbine rotors subjected to temperatures of 650 °C. Their results show that the time to rupture has a maximum at 9% Cr at a low stress of 98 MPa.

3. Basic methods of strengthening steels at elevated temperatures

The basic methods by which creep-resistant steels can be strengthened are solute hardening, precipitation or dispersion hardening, dislocation hardening and boundary or sub-boundary hardening [7–9]. It is possible to combine several strengthening mechanisms but it is often difficult to quantify the contribution of each to the overall creep strength.

3.1. Solute hardening

Taking the Hume–Rothery size effect and the high solid solubility in iron into account, substitutional solute atoms such as Mo and W, which have much larger atomic sizes than that of solvent iron, have been favored as solid solution hardeners for both ferritic and austenitic creep-resistant steels. The solid solution hardening due to Mo and W is practically superimposed on other strengthening mechanisms, e.g. precipitation hardening.

3.2. Precipitation or dispersion hardening

To achieve sufficient strengthening by this method, creep-resistant steels usually contain several types of carbonitrides.
and intermetallic compounds in the matrix and at grain boundaries: carbonitrides including M\textsubscript{23}C\textsubscript{6}, M\textsubscript{6}C, M\textsubscript{2}C\textsubscript{3}, MX and M\textsubscript{2}X, where M denotes a metallic element, and X is carbon and/or nitrogen atoms; and intermetallic compounds such as the Fe\textsubscript{2}(Mo,W) Laves phase, Fe\textsubscript{7}W\textsubscript{8} \chi phase, or \chi phase. In the special case of oxide-dispersion-strengthened (ODS) steels \[10\], fine particles of alloy oxides such as Y\textsubscript{2}O\textsubscript{3} are dispersed in the matrix by mechanical alloying. The dispersion of fine precipitates stabilizes free dislocations and the subgrain structure against recovery, which further enhances dislocation hardening and sub-boundary hardening, respectively.

Several mechanisms have been proposed for the threshold stress, corresponding to the stress required for a dislocation to pass through precipitate particles, such as the Orowan mechanism, local climb mechanism, general climb mechanism and Srolovitz mechanism \[11\]. The Orowan stress \(\sigma_{\text{Orowan}}\) is given by \[7\]

\[
\sigma_{\text{Orowan}} = 0.8 M G b / \lambda, \tag{1}
\]

where \(M\) is the Taylor factor \((=3)\), \(G\) is the shear modulus, \(b\) is the magnitude of the Burgers vector and \(\lambda\) is the mean interparticle spacing. Typical values of the volume percent, diameter and spacing of the major particles contained in tempered martensitic 9–12\% Cr steels after tempering are listed in table 1, together with the Orowan stress estimated from the values of interparticle spacing \[7\].

### 3.3. Dislocation hardening

Dislocation hardening given by \[7\]

\[
\sigma_{\text{p}} = 0.5 M G b (\rho_{\text{f}})^{1/2}, \tag{2}
\]

where \(\rho_{\text{f}}\) is the free dislocation density in the matrix, is an important strengthening mechanism in steel at ambient temperatures. Tempered martensitic 9–12\% Cr steels usually contain a high density of dislocations even after tempering, usually in the range of 1–10 \(\times\) \(10^{11}\) \text{m}^{-2}, in the matrix \[7, 12\].

At elevated temperatures, cold working enhances softening by promoting the recovery of excess dislocations and the recrystallization of the deformed microstructure, causing a loss of creep strength \[13\]. Dislocation hardening is useful for creep strengthening in the short term but it is not useful for increasing long-term creep strength at elevated temperatures.

### 3.4. Sub-boundary hardening

(9–12\%) Cr steels subjected to normalizing and tempering heat treatment are usually observed to have a tempered martensitic microstructure, which consists of laths and blocks with a high density of dislocations and fine carbonitrides dispersed along the lath and block boundaries and in the matrix. The laths and blocks can be regarded as elongated subgrains. The lath and block boundaries results in sub-boundary hardening given by \[7\]

\[
\sigma_{\text{sg}} = 10 G b / \lambda_{\text{sg}}, \tag{3}
\]

where \(\lambda_{\text{sg}}\) is the short width of the elongated subgrains.

\(\lambda_{\text{sg}}\) is the mean subgrain width, corresponding to the width of a lath, in the range of 0.3–0.5 \(\mu\)m in 9–12\% Cr steels after tempering. Using the values of \(G = 64\) GPa at 650°C, \(b = 0.25\) nm and \(\lambda_{\text{sg}} = 0.3–0.5\) \(\mu\)m, we obtain \(\sigma_{\text{sg}}\) = 530–320 MPa, which is much larger than the Orowan stress in table 1 for Fe\textsubscript{2}(W,Mo), M\textsubscript{23}C\textsubscript{6} and MX. As will be described later, the sub-boundary hardening enhanced by the fine distribution of precipitates along boundaries is the most important method for increasing the long-term creep strength of tempered martensitic 9\% Cr steel.

The coarsening of the laths and blocks with creep strain, which mainly takes place in the tertiary or acceleration creep region \[14, 15\] and causes an increase in \(\lambda_{\text{sg}}\) of equation (2), indicates the mobile nature of lath and block boundaries under stress. In the acceleration creep of tempered martensitic 9\% Cr steels, the progressive local coalescence of two adjacent lath boundaries near the Y-junction causes the movement of the Y-junction, resulting in the coarsening of the laths \[16\]. It is well known that polygon and subgrain boundaries free from precipitates in pure metals and solid solution alloys are highly mobile under applied stress \[17\]. The movement of lath and block boundaries can absorb or scavange excess dislocations from inside the laths and blocks. This corresponds to a dynamic recovery process, resulting in softening.

Figure 2 shows the effect of the addition of W on the creep rupture strength of 9Cr-(0–4)W-0.1C steels at 550, 600 and 650°C, together with that on the coarsening of M\textsubscript{23}C\textsubscript{6} carbides and laths during creep at 600°C \[16, 18\]. The creep rupture strength linearly increases with increasing W concentration up to about 3\%, at which the steel consists of 100\% tempered martensite. The creep rupture strength saturates above 3\% W, because the steel consists of tempered martensite and \(\delta\)-ferrite containing about 3 and 6\% W, respectively, and the volume fraction of \(\delta\)-ferrite increases with increasing total W concentration. It should be noted that the addition of W suppresses the coarsening of M\textsubscript{23}C\textsubscript{6} carbides and lath subgrains, although the mechanism by which this occurs is not fully understood \[19\]. Therefore, the addition of W enhances the precipitation hardening due to M\textsubscript{23}C\textsubscript{6} carbides, as given by equation (1) for the Orowan stress, which enhances the sub-boundary hardening, given by equation (2), because the M\textsubscript{23}C\textsubscript{6} carbides are distributed along the lath, block and packet boundaries and the prior austenite grain boundaries (PAGBs). It should also be noted that the contribution of W to the improvement of creep strength in the range below 3 mass\% W decreases with increasing temperature: 44, 30 and 11 MPa/mass\% W at 550, 600 and 650°C, respectively. This suggests that the strengthening mechanisms due to W originate from solid solution hardening.
Figure 2. Creep rupture strength and coarsening of M$_{23}$C$_{6}$ carbides and laths or subgrains of 9Cr-(0–4)W-0.1C steels as a function of W concentration [16, 18].

precipitation hardening and sub-boundary hardening, and that the occurrence of precipitation hardening and sub-boundary hardening decreases with increasing temperature due to coarsening. Figure 3 shows micrographs taken by transmission electron microscope (TEM) for 9Cr-1W-0.1C and 9Cr-4W-0.1C steels after creep rupture testing at 600 °C for about 2000 h. The dense distribution of M$_{23}$C$_{6}$ carbides along the lath and block boundaries in the 9Cr-4W-0.1C steel is correlated with the suppression of lath coarsening described above. In the 9Cr-1W-0.1C steel with a sparse distribution of M$_{23}$C$_{6}$ carbides along the lath boundaries, extensive coarsening of the laths takes place by the migration of lath and block boundaries, leaving large precipitates of M$_{23}$C$_{6}$ carbides in the matrix. This suggests that sub-boundary hardening is closely correlated with the distribution of precipitates along lath boundaries.

3.5. Mechanisms of creep strength loss in 9–12% Cr steels

An important criterion for the creep resistance of power plant steels is usually the $10^5$ h creep rupture strength at the operating temperature. The $10^5$ h creep rupture strength is defined as the stress at which a specimen deforms gradually with time so that creep rupture eventually occurs at $10^5$ h. The target value for the $10^5$ h creep rupture strength for the development of new steels is usually 100 MPa at the operating temperature.

In recent years, effort has been made to clarify the mechanisms of creep strength loss in tempered martensitic 9–12% Cr steels at 550 °C and above. The loss of creep strength often takes the form of a sigmoidal inflection in creep rupture data after long operating times. The proposed mechanisms mainly relate to the localized loss of precipitation hardening during creep [7]. The loss of precipitation hardening accelerates microstructure evolution causing the coarsening of the laths and blocks, resulting in the loss of sub-boundary hardening.

The precipitation of a Z phase, M$_6$X carbonitrides and the Fe$_2$(W,Mo) Laves phase during creep causes a loss of long-term creep strength, because such phases consume existing fine precipitates or solute-hardening atoms [20, 21]. The Z phase is a complex nitride of the form Cr(Nb,V)N. The precipitation of the Z phase takes place after a long time at the service temperature, and large particles are sometimes formed at the expense of previously existing fine vanadium nitrides, which leaves a vanadium-nitride free zone around
creep, similarly to Al. The analysis of creep data for the nine heats of tempered martensitic 12Cr-1Mo-1W-0.3V steel, given in NIMS Creep Data Sheets, indicates that the time to rupture decreases simply with decreasing available nitrogen concentration at low stress and long-term conditions [26]. The different heats correspond to different ingots and different products. The available nitrogen concentration is defined as the concentration of nitrogen free from AlN and TiN, given by total nitrogen concentration—Al–Ti (at.%). A higher Al content results in a lower available nitrogen concentration.

The recovery of the martensitic microstructure accelerated by the coarsening of \(M_{23}C_6\) carbides near PAGBs [27] and the \(Fe_2W\) Laves phase [6], the loss of creep ductility [7], the recovery of excess dislocations resulting from low-temperature tempering [28], and the inhomogeneous microstructure recovery due to the presence of \(\delta\)-ferrite [29, 30] have also been proposed as mechanisms of long-term creep strength loss in 9–12% Cr steels.

4. Tempered martensitic microstructure and precipitate design of 9% Cr steel

4.1. Tempered martensitic microstructure

Tempered martensitic 9–12% Cr steels such as P91, P92 (9Cr-0.5Mo-1.8W-VNb steel) and P122 (11Cr-0.4Mo-2W-CuV Nb steel), where P denotes pipe, used for thick section boiler components contain 0.05–0.1% carbon and about 0.05% nitrogen, which precipitate as \(M_{23}C_6\) carbides rich in Cr and/or MX carbonitrides rich in V and Nb during tempering. Figure 5 shows TEM micrographs of a replica near a PAGB and a thin film of 9Cr-3W-3Co-0.2V-0.05Nb steel containing 0.078% carbon and 0.05% nitrogen after tempering [31]. The microstructures shown are also typical for the microstructures of P91, P92 and P122.

The micrograph of the thin film shows that the microstructure consists of lath martensite which contain a high density of dislocations and fine precipitates. The micrograph of the replica shows that a large number of \(M_{23}C_6\) carbides and MX carbonitrides are distributed along the PAGB. The size of \(M_{23}C_6\) carbides after tempering is usually much larger in the vicinity of PAGBs, about 100–300 nm, than that inside grains, 50–70 nm. The size of MX carbonitrides, 5–20 nm, is much smaller than that of \(M_{23}C_6\) carbides. The MX carbonitrides are distributed at laths, blocks, packet boundaries and PAGBs as well as in the matrix within laths, while most of the \(M_{23}C_6\) carbides are distributed along laths, blocks, packet boundaries and PAGBs [31–33]. Figure 6 shows the lath martensitic microstructure, showing the distribution of \(M_{23}C_6\) carbides and MX carbonitrides in 9% Cr steel [31]. The \(M_{23}C_6\) carbides and MX carbonitrides further increase in size during creep at elevated temperatures by the mechanism of Ostwald ripening, because most of the carbon and nitrogen atoms in the supersaturated solid solution of the steels precipitate as carbides and nitrides, respectively, during tempering before creep tests. We have revealed that the coarsening rate of \(M_{23}C_6\) carbides is much greater in the vicinity of PAGBs than within grains [27, 31], because of enhanced diffusion along the PAGBs. This suggests that the
long-term stabilization of fine precipitates, particularly those near PAGBs, is a key issue for suppressing the loss of creep strength.

4.2. Precipitate design

Bhadeshia pointed out that in multiphase systems, such as creep-resistant 9–12% Cr steels, the coarsening behavior of precipitates is greatly affected by the presence of other phases [19]. In the following, for simplicity, we will describe the type of precipitate phases that are the most appropriate for preventing coarsening during exposure at elevated temperatures, based on Fe–M–C alloys, where M is an alloy element. The volume-diffusion-controlled Ostwald ripening of M6C carbides in Fe–M–C alloys is given by [34]

\[ r^3 - r_0^3 = k_3 t, \]

\[ k_3 = 8(a + b)\sigma V D_M u_M / 9aRT (u_pM - u_M)^2, \]

where \( r \) and \( r_0 \) are the average particle radii at the times \( t \) and \( t = 0 \), respectively, \( \sigma \) is the interfacial energy of the carbides, \( V \) is the molar volume of the carbides, \( D_M \) is the volume-diffusion coefficient of metal \( M \), \( u_M \) and \( u_{pM} \) are the concentrations of \( M \) in the matrix and carbides, respectively, \( R \) is the gas constant and \( T \) is the temperature. The main factors affecting the coarsening rate of precipitate particles are the volume-diffusion coefficient, the solid solubility of participating elements and the interfacial energy. We have evaluated the volume-diffusion coefficient and the solid solubility of alloying elements in iron. The impurity volume-diffusion coefficients in iron are not significantly different, less than one order of magnitude, among different elements such as W, Mo, V and Nb [35]. On the other hand, the solid solubility of alloying elements, which are in equilibrium with their carbides, nitrides and the Fe2(Mo,W) Laves phase in Fe–M–0.1%C ternary, Fe–M–0.05%N ternary and Fe-M binary alloys, respectively, is evaluated using Thermo-calc, the results of which are shown in figure 7. The solid solubility of V, Nb and Ti in equilibrium with their nitrides in Fe–M–0.05%N alloys is very low. It should be noted that TiN is extremely stable up to its melting temperature, because of its extremely low solid solubility in iron up to its melting temperature. This indicates that we cannot control the dispersion of fine TiN by appropriate heat treatment, such as solution treatment and subsequent aging or tempering. Thus, TiN is excluded from consideration in the present precipitate design. The carbides and nitrides of V and Nb and the carbides of Ti are the most appropriate candidates, because they exhibit a very low coarsening rate during exposure at
Elevated temperatures. However, the addition of carbon to a 9% Cr steel causes the formation of a large amount of $M_23C_6$ carbides rich in Cr. Wey et al. [34] reported that the coarsening rate of Cr carbides in iron was much larger than that of V and Nb carbides at elevated temperatures. Therefore, it is crucial for the carbon concentration of 9% Cr steel to be reduced to a very low level, so as to promote the formation of MX nitrides as very fine and thermally stable particles to enable prolonged periods of exposure at elevated temperatures and to eliminate unstable Cr-rich $M_23C_6$ carbides [36, 37].

The Thermo-calc evaluation of equilibrium phases in a 9Cr-3W-3Co-0.2V-0.05Nb-0.05N steel during tempering at 800 °C is shown in figure 8 as a function of carbon concentration. Three types of precipitate phases, $M_23C_6$ carbides, MX carbonitrides and the Fe$_2$W Laves phase, appear as equilibrium precipitate phases at 800 °C. However, the Fe$_2$W Laves phase does not precipitate in this steel during tempering at 800 °C for 1 h, because of the short tempering time. Therefore, the Fe$_2$W Laves phase is omitted from figure 8. The changes in the amounts of $M_23C_6$ and MX with carbon concentration at a creep test temperature of 650 °C are similar to those at 800 °C. The amount of $M_23C_6$ carbides rich in Cr decreases with decreasing carbon concentration, while the amount of MX carbonitrides is approximately constant over a wide range of carbon concentration from 0 to 0.15%. The amount of MX carbonitrides is larger than that of $M_23C_6$ carbides at low carbon concentrations below 0.02%. The MX carbonitrides mainly consist of vanadium nitrides and a small amount of niobium carbides, suggesting that the MX carbonitrides are substantially vanadium nitrides. This indicates that we can almost exclusively obtain vanadium nitrides after tempering by the reducing carbon concentration to very low amounts below 0.02%.

In the present research, the use of finely dispersed thermally stable precipitates to prevent coarsening and its effect on creep strength have been examined for a tempered martensitic 9% Cr steel on the basis of the following scenarios.

(a) Elimination of unstable $M_23C_6$ carbides and dispersion of only nanosize MX carbonitrides by reducing carbon concentration.

(b) Reduction of coarsening rate of $M_23C_6$ carbides near PAGBs using boron.

(c) Combination of coarsening-resistant $M_23C_6$ carbides and nanosize MX carbonitrides.

5. Improvement of creep strength by dispersion of nanosize carbonitrides

5.1. Elimination of unstable $M_23C_6$ carbides and dispersion of only nanosize MX carbonitrides and the effect on creep strength

On the basis of the estimation shown in figure 8, elimination of unstable $M_23C_6$ carbides and the dispersion of nanosize MX nitrides were examined using 9Cr-3W-3Co-0.2V-0.05Nb-0.05N (mass%) steel with different carbon concentrations of 0.002, 0.018, 0.047, 0.078, 0.120 and 0.160%. A large number of fine precipitate particles having a size of less than 10 nm are distributed along boundaries such as PAGBs and the lath, block and packet boundaries of the steel with 0.002% C after tempering, as shown in figure 9. This is considerably different from the microstructure of the steel with 0.078% C shown in figure 5, where large particles of $M_23C_6$ carbides of 100 to 300 nm size are distributed along the PAGBs together with fine particles of MX carbonitrides. The fine precipitate particles in figure 8 were identified as MX carbonitrides and were confirmed via energy-dispersive microanalysis to be rich in V and Nb [37]. No Cr nitride was detected. The spacing between the (111) planes of the MX particles was measured from a
photograph of the diffraction pattern to be about 0.2398 nm, which corresponds with that of vanadium nitride, 0.2390 nm. The orientation relationship is given by (100)\textsubscript{MX}/(100)\textsubscript{ferrite}, [010]\textsubscript{MX}/[011]\textsubscript{ferrite}, [001]\textsubscript{MX}/[011]\textsubscript{ferrite}. Consequently, the MX nitrides shown in figure 9 satisfy the Baker–Nutting relationship. The dense distribution of fine particles along the boundaries causes a significant decrease in the interparticle distance. The fine MX carbonitride particles were also distributed in the matrix within laths in addition to along the boundaries.

The time to rupture and the minimum creep rate of the steel at 650 °C and 140 MPa are shown in figure 10 as a function of carbon concentration. The time to rupture is substantially independent of carbon concentration for higher carbon concentrations above 0.047% but it significantly increases for concentrations below 0.018%, which is also typical for applied tensile stresses within the range of 140–200 MPa. On the other hand, the minimum creep rate significantly decreases for carbon concentrations below 0.018%. Comparing these results with those in figure 8, it is evident that the creep strength of 9% Cr steel is significantly improved by the elimination of M\textsubscript{23}C\textsubscript{6} carbides and the dispersion of nanosize MX nitrides.

5.2. Creep-strengthening mechanism

Figure 11 shows a comparison of creep rate versus time curves between the two representative steels in figure 10 with 0.002 and 0.078% C at 650 °C and 140 MPa. The carbon concentration of 0.078% is similar to that in conventional 9% Cr steels such as P92 and P91. 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. Many researchers have shown that for tempered martensitic steels there is an ever-evolving microstructure and that the change in creep rate reflects coupled elementary processes, such as micrograin growth, and changes in dislocation density, precipitate volume fraction and size [14, 15, 38–41]. These results suggest that in tempered martensitic steels there is no dynamic microstructural equilibrium during creep, which characterizes the steady-state creep of simple metals and alloys. In figure 11, the creep rates in the initial stage are lower in the steel with 0.002% carbon than in the steel with 0.078% carbon. The decrease in creep rate with time in the transient creep region, corresponding to the slope of the creep rate curves, is substantially the same for the two steels. It should be noted that the minimum creep rate of the steel with 0.002% carbon is about 1/10 of that of the steel with 0.078% carbon, while the time to rupture of the steel with 0.002% carbon is about 10 times that of the steel with 0.078% carbon. Usually, the time to rupture is inversely proportional to the minimum creep rate. This is known as the Monkman-Grant relationship. The longer time to rupture observed by reducing the carbon
concentration results from a decrease in the minimum creep rate. A decrease in the creep rate in the transient region is also observed upon the precipitation of MX carbonitrides [40, 42], a FePd-L1$_2$ intermetallic compound [43] and the Fe$_3$W Laves phase [41] from a supersaturated solid solution of 9% Cr steel.

We have 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 evolution [14]. We have also suggested that 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 figure 11, the lower value of the initial creep rate in the steel with 0.002% carbon than that in the steel with 0.078% carbon results from greater precipitation strengthening after tempering. However, the difference in the initial creep rate between the two steels is only slight, 1/3 order of magnitude, which is much smaller than the difference in the minimum creep rate between the two steels. On the other hand, the onset of acceleration creep is retarded to a later time in the steel with 0.002% carbon, which decreases the minimum creep rate.

Whereas the density of precipitates along boundaries is much higher in the steel with 0.002% carbon than in the steel with 0.078% carbon as described above, the density of MX carbonitrides in the matrix within the laths is lower in the steel with 0.002% carbon than in the steel with 0.078% carbon: 5.5 $\times$ 10$^{13}$ and 7.5 $\times$ 10$^{13}$ m$^{-2}$ for the steels with 0.002 and 0.078% carbon, respectively [37]. This is because the amount of MX carbonitrides along the boundaries is much larger in the steel with 0.002% carbon than in the steel with 0.078% carbon, since there are no M$_{23}$C$_6$ carbides in the steel with 0.002% carbon. On the other hand, most of the MX carbonitrides in the steel with 0.078% carbon are distributed in the matrix and only a small amount of MX carbonitrides are distributed along the boundaries together with a large amount of M$_{23}$C$_6$ carbides. The fine MX carbonitrides in the matrix act as obstacles to dislocation movement to lath and block boundaries, which reduces the number of dislocation annihilations and decreases the creep rate, as illustrated in figure 12. At lath and block boundaries, the climbing and redistribution of dislocations in the boundary wall are prohibited when dense distributions of MX and M$_{23}$C$_6$ in the boundary wall act as obstacles, which decreases the efficiency of dislocation absorption at the boundaries. This also reduces the number of dislocation annihilations and decreases the creep rate. On the basis of the results described above, the creep rate in the transient region is given by

$$\dot{\varepsilon} = \rho_i v_s b \eta,$$

where $\rho_i$ is the free dislocation density in the matrix within the laths, $v_s$ is the velocity of free dislocations in the matrix, $b$ is the magnitude of the Burgers vector and $\eta$ is the efficiency of dislocation absorption at boundaries. The present results of lower creep rates in the steel with 0.002% carbon than in the steel with 0.078% carbon in the transient region suggest that the lower $\eta$ in the steel with 0.002% carbon due to fine distribution of MX carbonitrides along the boundaries is the main factor causing the lower creep rate in the transient region rather than precipitation strengthening due to fine MX carbonitrides in the matrix. The agglomeration and coarsening of precipitates at the boundaries during transient creep promote the climbing and redistribution of dislocations in the boundary walls, resulting in an increase in the efficiency of dislocation absorption at the boundaries. The absorption of dislocations at the boundaries accelerates further agglomeration and coarsening of the precipitates and also promotes the climbing and redistribution of dislocations in the boundary walls. These chain reactions increase the migration of lath or block boundaries, promoting the onset of acceleration creep. The observed significant decrease in the minimum creep rate by reducing the carbon concentration is explained mainly by the retardation of the onset of acceleration creep, resulting from the stabilization of the lath-block microstructure during creep. The present results suggest that sub-boundary hardening enhanced by fine distributions of precipitates along the lath and block boundaries is the main strengthening mechanism in the present 9% Cr steel.

The increase in nitrogen concentration from 0.05% in the steel with 0.002% carbon to 0.07 or 0.10% increases the amount of MX carbonitrides but decreases the creep strength at 650 $^\circ$C [44]. After tempering, large Cr$_2$N particles as well as fine MX nitrides were distributed along the lath, block and packet boundaries and PAGBs in the high nitrogen steels with 0.07 or 0.10% nitrogen, although the amount of Cr$_2$N was small. The large Cr$_2$N particles occupied part of the precipitation sites of fine MX nitrides, resulting in an increase in mean interparticle spacing along the boundaries. During creep at 650 $^\circ$C, the agglomeration and coarsening rates of MX nitrides are greater in the higher-nitrogen steels. Furthermore, the formation of a Z phase takes place after shorter times in the higher-nitrogen steels during creep at 650 $^\circ$C. These promote the onset of acceleration creep in the higher-nitrogen steels, which results in a higher minimum creep rate and a shorter time to rupture in the higher-nitrogen steels.

Figure 12. Schematic illustration of lath and block microstructure.

(a) Lath & block boundaries (b) Lath & block boundaries
The dispersion of nanosize TiC carbides also results in a significant decrease in the minimum creep rate and a significant increase in the time to rupture of 9% Cr steel [45]. To utilize TiC in 9% Cr steel, however, it is crucial to reduce the nitrogen concentration to a very low level, so as to promote the formation of very fine and thermally stable TiC particles and also to eliminate TiN.

6. Improvement of creep strength by stabilization of fine M23C6 carbides near PAGBs using boron

6.1. Stabilization of fine M23C6 carbides near PAGBs using boron and its effect on creep strength

The effect of boron on the fine distribution of M23C6 carbides has been examined for tempered martensitic 9Cr-3W-3Co-0.2V-0.05Nb-0.08C steel containing boron with concentrations of 0, 48, 92 and 139 ppm. Nitrogen was not added to the steel to avoid the formation of boron nitride BN during normalizing heat treatment at high temperatures. Therefore, only M23C6 carbides and no MX carbonitride 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 M23C6 carbides in the vicinity of the PAGBs, as shown in figure 13(a) [46]. The enrichment of boron in M23C6 carbides is also observed after tempering, but it becomes more significant with increasing aging time. The enrichment of boron in M23C6 carbides has already been reported for 9 to 12% Cr steels by the chemical analysis of electrolytically extracted residues [47] and also by atom probe field ion microscopy [48, 49]. However, whether or not the M23C6 carbides, in which boron was enriched, were located in the vicinity of the PAGBs was not specified. In the present study, no evidence is found for the enrichment of boron in the Fe3W Laves phase, which precipitated during exposure at elevated temperatures. The fine distribution of M23C6 carbides along the PAGBs is maintained in the steel with 139 ppm boron during exposure at elevated temperatures as shown in figure 13(b) [27, 50]. In the base steel without boron, a fine distribution of M23C6 carbides is observed after tempering but extensive coarsening takes place in the vicinity of the PAGBs during exposure at elevated temperatures. This indicates that the addition of boron reduces the rate of the Ostwald ripening of M23C6 carbides in the vicinity of PAGBs during exposure at elevated temperatures.

Figure 14 shows the effect of boron on the creep rupture strength of 9Cr-3W-3Co-0.2V-0.05Nb-0.08C steel at 650 °C. The base steel without boron exhibits a loss of creep rupture strength after about 1000 h at 650 °C. With increasing boron content, however, the long-term loss of creep rupture strength becomes less pronounced and the time to rupture significantly increases at low stresses, although the addition of boron scarcely affects the time to rupture at high stresses. The creep rupture strength of the steel with 139 ppm boron is slightly higher than that of the other steels at high stresses. This is not due to the effect of boron but to the slightly higher nitrogen content in the steel with 139 ppm boron than in the other steels. The residual nitrogen contents were 19, 11, 16 and 34 ppm in the steels with 0, 48, 92 and 139 ppm boron, respectively. The extremely low nitrogen content in the base steel without boron suggests an extremely low amount of MX carbonitrides and hence an extremely low driving force for the formation of the Z phase during creep. Therefore, the dissolution of fine MX carbonitrides and the precipitation of the Z phase can be excluded from the explanation for the loss of creep rupture strength.

Takahashi et al [47] reported that for 0.2C-10.5Cr-1.5Mo-0.2V-0.2Nb-0.02N steel, the addition of 120 to 370 ppm boron improved the creep rupture strength at 650 °C. They observed that boron was enriched in M23C6 carbides and that the distribution of M23C6 carbides in the steel with boron was finer than that in the steel without boron. In Europe,
9–12% Cr steels containing a high boron concentration of 100 ppm or more are considered to be promising for use in next-generation steam turbines and the main steam pipes in USC power plants at 625 to 650 °C [51, 52].

The effect of boron on creep deformation behavior is shown in figure 15(a), where the creep rate versus time curves of the steels at 650 °C and 80 MPa are shown. The initial creep rates are approximately the same among the steels containing different boron contents, except for the steel with 139 ppm boron, which exhibits a slightly lower creep rate. This is again due to the slightly higher nitrogen content in the steel with 139 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, which is different from the effect of dispersed nanosize MX carbonitrides described in the previous section, but it significantly decreases the minimum creep rate by retarding the onset of acceleration creep.

On the basis of the results described above, figure 15(b) shows the mechanism responsible for the improvement of time to rupture by the addition of boron. Because no nitrogen is added, only $M_23C_6$ carbides are distributed along the lath, block and packet boundaries and PAGBs. Because the $M_23C_6$ carbides are approximately the same size among the steels containing different boron contents after tempering, the steels have substantially the same creep rates in the initial creep stage. However, the high coarsening rate of $M_23C_6$ carbides in the vicinity of the PAGBs of the steels containing lower boron contents during creep promotes the climbing and redistribution of dislocations in the boundary walls (see figure 12), which increases the efficiency of dislocation absorption at the boundaries, as described in section 5.2. This 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 [50, 53]. The sub-boundary hardening enhanced by $M_23C_6$ carbides is the most important factor in long-term creep strengthening. Although the $M_23C_6$ carbides near the PAGBs are much larger than those at the center of grains (see figure 13(b)) and also much larger than the MX particles along the boundaries (see figure 9), the suppression of particle coarsening during creep and the maintenance of a homogeneous distribution of less fine $M_23C_6$ carbides near the PAGBs, which are precipitated during tempering, are very effective for avoiding the degradation in creep strength and for improving long-term creep strength.

**Figure 14.** Effect of boron on creep rupture strength of 9Cr-3W-3Co-0.2V-0.05Nb-0.08C steel at 650 °C.

**Figure 15.** (a) Creep rate versus time curves of the steels at 650 °C and 80 MPa and (b) schematic illustrations showing mechanism of effect of boron for improvement of time to rupture.

6.2. Mechanisms for enrichment of boron in $M_23C_6$ near PAGBs and for reduction of coarsening rate of $M_23C_6$ using boron

In the iron-carbon-boron ternary phase diagram at 900 °C, $Fe_{23}(CB)_6$ appears in alloy compositions containing several % boron [54]. Because the maximum concentration of boron in the present steels is only 139 ppm, $Fe_{23}(CB)_6$ cannot...
After achieving equilibrium grain size, we obtain the concentration of boron at grain boundaries ($C_{GB}$) and inside grains ($C_0$) as a function of temperature.

Initially, boron is assumed to be distributed homogeneously with concentration $C_i$ throughout the specimen, as illustrated in figure 16(a). After achieving equilibrium grain boundary segregation, the concentration of boron at the grain boundaries $C_{GB}$ is described as

$$C_{GB} = C_0 \exp \left( \frac{B}{RT} \right),$$

where $C_0$ is the concentration of boron within the grains, $B$ is the binding energy between the boron and grain boundaries, $R$ is the gas constant and $T$ is the absolute temperature. Because the summation of the number of boron atoms at the grain boundaries and that within the grains is equal to the total number of boron atoms, with the assumption of a two-dimensional grain structure we obtain

$$\pi r_0^2 C_0 + \pi (r_0 - \delta)^2 C_0 = \pi r_0^2 C_i$$

where $r_0$ is the radius of a grain, $\delta$ is the width of a grain boundary, and $C_i$ is the initial boron concentration. From equations (7) and (8), we obtain

$$C_0 = \frac{\pi r_0^2 C_i}{[\pi r_0^2 - \pi (r_0 - \delta)^2] \exp \left( \frac{B}{RT} \right) + \pi (r_0 - \delta)^2}.$$  

Using a binding energy of 62.7 kJ mol$^{-1}$ [55] between boron and grain boundaries reported for type 316 stainless steel, figure 16(b) shows the concentrations of boron at the grain boundaries ($C_{GB}$) and inside the grains ($C_0$) as a function of temperature, where the initial boron concentration and the grain size are assumed to be 100 ppm and 50 $\mu$m, respectively. At a normalizing temperature of 1100 °C, the segregation of several % boron can be achieved at the grain boundaries.

The enrichment process of boron in M$_{23}$C$_6$ is schematically shown in figure 17. First, during normalizing heat treatment at 1100 °C, only the grain boundary segregation of boron takes place, and there is no precipitation of M$_{23}$C$_6$ carbides because of the high temperature. The segregation of boron at the grain boundaries is estimated to be several % as described above. During subsequent tempering at 800 °C, the precipitation of M$_{23}$C$_6$ carbides can take place preferentially at grain boundaries and lath, block and packet boundaries. Because the segregation of boron at grain boundaries is also achieved, the enrichment of boron in M$_{23}$C$_6$ to form M$_{23}$C$_6$ takes place in the vicinity of PAGBs. During creep at 650 °C, the enrichment of boron in M$_{23}$C$_6$ is more significant because of the lower temperature.

Although the reduction of the coarsening rate of M$_{23}$C$_6$ carbides in the vicinity of PAGBs is considered to be correlated with the enrichment of boron in the M$_{23}$C$_6$ carbides near the PAGBs and also with the segregation of boron at grain boundaries, detailed mechanisms are not clear at present. An experimental investigation to clarify the effect of boron on the diffusion coefficient, solid solubility and interfacial energy in equations (4) and (5) and the effect of the presence of other phases will be required in future.
As described above, soluble boron contributes to the enrichment in $\text{M}_2\text{C}_6$ carbides and soluble nitrogen causes the precipitation of nanosize MX carbonitrides. Large boron nitride particles having a size of 1 $\mu$m 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 of boron and nitrogen. Figure 18(a) shows the relationship between boron and nitrogen concentrations and the size of boron nitride particles formed in various 9 to 12% Cr steels at normalizing temperatures of 1050 to 1150 °C [56]. The solubility product for boron nitride at 1050 to 1150 °C is given by

$$\log[B] = -2.45\log[N] - 6.81$$  (10)

where [%B] and [%N] are the concentrations of soluble boron and soluble nitrogen in mass%, respectively. At a boron concentration of 139 ppm, only 95 ppm nitrogen can dissolve in the matrix without the formation of any boron nitride during normalizing. Figure 18(b) shows the enrichment of boron in $\text{M}_2\text{C}_6$ carbides in a steel containing 144 ppm boron and 650 ppm nitrogen. The enrichment of boron in $\text{M}_2\text{C}_6$ carbides is much less than that in the steel containing 139 ppm boron and 34 ppm nitrogen in figure 13(a), because the formation of boron nitride during normalizing consumes most of the soluble boron, as shown by the arrow in figure 18(a) and only a small amount of boron contributes to the enrichment in $\text{M}_2\text{C}_6$ carbides.

The effect of nitrogen addition of 15, 34, 79, 300 and 650 ppm on the creep rupture strength was examined for 9Cr-3W-3Co-0.2V-0.05Nb-0.08C steel containing 140 ppm boron. The creep rupture strength significantly increases with increasing nitrogen content from 15 to 79 ppm, but the excess addition of nitrogen, such as 300 and 650 ppm, decreases the creep rupture strength under short-term conditions. Figure 19 shows the nitrogen concentration dependence of the time to rupture and the minimum creep rate at 650 °C and 120 MPa. 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 139 ppm boron at a normalizing temperature of 1100 °C, as shown in figure 19(a). 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.

Figure 20 shows the creep rupture data for several tempered martensitic 9–12% Cr steels used for boilers. MARN (Martensitic 9% Cr steel strengthened by MX nitrides) and MARBN (Martensitic 9% Cr steel strengthened by boron and MX nitrides) are the names we hereafter use for the 9% Cr steel with 0.002% carbon shown in figures 10 and 11 and the 9% Cr steel with 139 ppm boron and 79 ppm
The creep-fatigue life. The addition of boron without and  
are experimental steels that are being developed 
. Therefore, 
. The addition of boron 
this significantly improves resistance to oxidation of the present 9% Cr steel in steam at 650 °C.

8. Conclusion

Dispersed fine vanadium nitrides having a size of less than 10 nm without M_{23}C_6 carbides is achieved along the lath, block and packet boundaries and also along the PAGBs of 9Cr-3W-3Co-0.2V-0.05Nb-0.05N steel by reducing the carbon concentration to 0.002%. The microstructure is different from that of conventional steels containing about 0.1% carbon, where large particles of M_{23}C_6 carbides of 100 to 300 nm size are distributed along the lath and block boundaries and PAGBs together with fine MX carbonitride particles along the boundaries and in the matrix. The time to rupture significantly increases for carbon concentrations below 0.018%, at which MX particles are dominant. The dispersed nanosize MX particles decrease the creep rate in the transient region and also the minimum creep rate. The sub-boundary hardening enhanced by the finely distributed MX precipitates along the lath and block boundaries is the main strengthening mechanism in the present 9% Cr steel. Dispersed nanosize titanium carbides with a minimized nitrogen content also significantly increase the creep strength at 650 °C.

The coarsening of M_{23}C_6 carbides near PAGBs promotes localized creep deformation there, which causes the degradation of long-term creep strength of 9Cr-3W-3Co-0.2V-0.05Nb-0.08C steel after 1000 h at 650 °C. The degradation becomes less pronounced with increasing boron concentration up to 139 ppm. The addition of boron does not decrease the creep rate in the transient region, which is different from the effect of the dispersed nanosize MX precipitates described above, but it significantly decreases the minimum creep rate by retarding the onset of acceleration creep through the suppression of the coarsening of M_{23}C_6 carbides near the PAGBs by the enrichment of boron in M_{23}C_6 near the PAGBs. Although the M_{23}C_6 carbides are much larger than the MX precipitates, the suppression of particle coarsening during creep and the maintenance of a homogeneous distribution of less fine M_{23}C_6 carbides near the PAGBs are very effective for avoiding the degradation of creep strength and for improving long-term creep strength.

The present 9% Cr steels, designated MARN and MARBN, exhibit higher creep strength at 650 °C than existing high-strength steels used for thick section boiler components.
Acknowledgments

I thank everyone participating in the Ultra-Steel Project at NIMS. I am also grateful to the members of the Creep Group at NIMS for their sincere efforts.

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