New martensitic steels

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10.1 Introduction

Energy security combined with lower carbon dioxide emissions are increasingly quoted to protect the global environment in the 21st century. Coal provides us abundant, low-cost resources for electric power generation. However, traditional coal-fired power plants have been emitting environmentally damaging gases such as CO₂, NOₓ, and SOₓ at high levels relative to other electric power generation options. 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. In Japan, coal-fired steam power plants have already extended to the USC conditions in the 1990s, which are based on materials technology accumulated for high-strength heat-resistant steels [1,2]. This enables the steam temperature to be raised to 610–620°C, as shown in Fig. 10.1.

In addition to enough creep strength, high operational flexibility is another issue for thick-section components in USC power plants. Martensitic steels of 9 to 12% Cr can offer the highest potential to meet the required flexibility because of their smaller thermal expansion and larger thermal conductivity than austenitic steels and Ni-base alloys.

The materials development projects for advanced ultra-supercritical (A-USC) power plants with steam temperature of 700°C or above have been performed to achieve a high efficiency in Europe [3,4], in the United States [5], in Japan [6], China [7], India [8], and so on. These projects involve the replacement of martensitic 9 to 12Cr steels with Ni-base alloys for the components subjected to the highest temperature. To minimize the requirement of expensive Ni-base alloys, martensitic 9 to 12Cr steels can be used for the components subjected to the next-highest temperatures, below 650°C [1]. Critical issues for the development of martensitic 9 to 12Cr steels for 650°C USC boilers are the improvement of oxidation resistance as well as long-term creep strength, including welded joints. In the A-USC project in Japan, the target values of 100,000 h creep rupture strength for candidate ferritic steels for thick-section boiler components are larger than 80 MPa at 650°C and larger than 0.7 of weld strength reduction factor at 650°C and 100,000 h [6].

This chapter comprehensively describes the development history of martensitic 9 to 12Cr steels in coal-fired power plants, the strengthening mechanisms and degradation behavior in creep of martensitic 9 to 12Cr steels, and the key metallurgy for achieving the improvement of long-term creep strength of base metal and welded joints for martensitic 9Cr steel at 650°C by microstructure stabilization near prior austenite grain boundaries (PAGBs). The improvement of oxidation resistance in steam at 650°C is achieved by pre-oxidation treatment in argon gas.
Materials for Ultra-Supercritical and Advanced Ultra-Supercritical Power Plants

10.2 Development history and utilization of 9 to 12Cr martensitic steels in coal power plants

Fig. 10.2 shows the development progress of martensitic boiler and turbine steels in Japan. The improvement of creep strength of martensitic 9 to 12Cr steels has been achieved by substituting a part or all of Mo with W and also by the addition of Co, Nb, nitrogen, and boron. The total concentration of alloying elements has been gradually increasing to improve the creep strength. The increase in ferrite-forming element W requires higher Co, which is an austenite stabilizing element, for the elimination of δ-ferrite. Three high-strength 9Cr steels of MARBN, Low-C 9Cr, and SAVE12AD are candidates in the A-USC project in Japan for the thick-section boiler components such as main steam pipes and headers operating at 650°C maximum [1,6]. The candidates for the highest temperature boiler components at around 700°C are Ni-base alloys. MARBN is a martensitic steel strengthened by boron and MX nitrides, which was alloy-designed on the base of the stabilization of martensitic microstructure in the vicinity of PAGBs [9]. Low-carbon 9Cr steel was alloy designed to stabilize the martensitic microstructure at elevated temperature, by minimizing impurities Ni and Al as low as possible [10]. The carbon concentration is also reduced to 0.035%, which improves weldability. SAVE12AD contains high boron but low nitrogen, similar to MARBN [11]. Original SAVE12 contained a high Cr concentration of 12%, but in SAVE12AD the Cr concentration is reduced to 9% to achieve long-term stabilization of martensitic microstructure [12].

MTR10A, HR1200, and TOS110 in Fig. 10.2 were developed by fabrication companies in Japan in the late 20th century before starting the A-USC project for application to turbine rotors with steam temperature of 630°C [13]. These rotor steels were originally intended to be used in 650°C-class USC power plants. At present, however, we have no 650°C-class USC power plant. Therefore, the rotor steels are
New martensitic steels

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<table>
<thead>
<tr>
<th>Main steam pipe &amp; header</th>
<th>Turbine rotor</th>
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<tr>
<td><strong>600°C class</strong>&lt;br&gt;ASME P91 (9Cr-1Mo-VNb)</td>
<td><strong>566°C class</strong>&lt;br&gt;GE (10.5Cr-1Mo-VNbN)</td>
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<tr>
<td><strong>620°C class</strong>&lt;br&gt;ASME P92* (9Cr-0.5Mo-1.8W-VNb)&lt;br&gt;ASME P122* (11Cr-0.4Mo-2W-CuVnbN)</td>
<td><strong>600°C class</strong>&lt;br&gt;TMK2* (10Cr-0.4Mo-1.8W-VNbN)&lt;br&gt;HR1100* (10.3Cr-1.2Mo-0.3W-VNbN)&lt;br&gt;TOS107* (10Cr-1Mo-1W-VNbN)</td>
</tr>
<tr>
<td><strong>650°C class</strong>&lt;br&gt;candidate for A-USC&lt;br&gt;MARBn* (9Cr-3W-3Co-VNbNB)&lt;br&gt;SAVE 12AD* (9Cr-2.9W-CoVnbTa-NdN)&lt;br&gt;Low-C 9Cr* (9Cr-2.4W-1.8Co-VNb)</td>
<td><strong>630°C class</strong>&lt;br&gt;candidate for A-USC&lt;br&gt;MTR10A* (10Cr-0.7Mo-1.8W-3Co-VnbB)&lt;br&gt;HR1200* (11Cr-2.6W-3Co-NvNbB)&lt;br&gt;TOS110* (10Cr-0.7Mo-1.8W-3Co-V nbB)</td>
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*developed in Japan

Figure 10.2 Development progress of martensitic boiler and turbine steels in Japan.

Now candidates in the A-USC project in Japan for the next-highest temperature rotors, operating at 630°C maximum. MTR10A, HR1200, and TOS110, which were developed as upgrade versions of TMK2, HR1100, and TOS107, respectively, are martensitic 10 to 11Cr steels containing high W, Co, and boron, similar as boiler steels MARBN, Low-C 9Cr and SAVE12AD.

In Europe, the development and evaluation of martensitic 9 to 12Cr steels for boiler and turbine of USC power plants have been continued within the frame of European COST programs, COST 501 (1986–1997), COST 522 (1998–2003), and COST536 (2004–2009), where COST means Cooperation in Science and Technology [14,15]. The target temperature of the steels to be developed was set to be 600, 620, and 650°C in the COST 501, COST 522, and COST 536 programs, respectively. The outcome of COST 522 was the demonstration of the manufacturability of large rotor forgings in the alloy with the highest potential for 620°C application, which is an FB2 steel (9Cr-1Mo-1Co-0.2V-0.07Nb-0.02N-100 ppm boron type). In the COST 536 program, on the base of the promising composition of FB2, the role of Nb and Ta in the long-term creep stability has been investigated using a trial melt FB2-3Ta (8.9Cr-1.49Mo-1.0Co-0.2V-0.003Nb-0.013B-0.009N-0.08Ta) with higher Si for steam oxidation resistance, a changed boron/nitrogen ratio, lowest Ni content, and replacement of a part of Nb by Ta [15]. The results of creep rupture testing at 650°C on a trial melt FB2-3Ta suggest that Ta in the chosen concentration would not be more effective than Nb compared to FB2.
Other strategies in Europe are that the characterization of 9Cr steel having the same chemical compositions as MARBN and the further optimization of MARBN are being conducted in several projects, UK Impact project [16], MACPLUS project [17], Energy Materials Working Group (WG2), and EMEP (engineered micro- and nanostructures for enhanced long-term high-temperature materials performance) [18,19]. Their objectives are to develop advanced MARBN for the long-term safe operation at 650°C.

In China, a martensitic 9Cr steel G115 was developed for pipe applications at 650°C or below and is now a candidate steel in the A-USC project in China [20]. The chemical composition of G115 is 9Cr-3W-3Co-1CuVNbB containing 150 ppm boron and 140 ppm nitrogen, similar to MARBN except for the addition of 1% Cu.

In the United States, there is no program on the development of new martensitic 9 to 12Cr steels in the US DOE/OCDO A-USC project. The strategy in the United States is to use existing martensitic 9 to 12Cr steels.

10.3 Basic methods of strengthening martensitic 9 to 12Cr steels in creep at elevated temperature

The basic methods in which creep-resistant steels can be strengthened are solid solution hardening, precipitation hardening, dislocation hardening, and boundary and sub-boundary hardening [21–23]. It is possible to combine several strengthening mechanisms, but it is often difficult to quantify the contribution of each mechanism to the overall creep strength. It becomes evident that the boundary and sub-boundary hardening is the most important strengthening mechanism in long-term creep of martensitic 9 to 12Cr steels and is enhanced by fine dispersion of precipitates along boundaries for up to long times. In the following, recent topics on the basic methods of strengthening martensitic 9 to 12Cr steels for power plants are described.

10.3.1 Solid solution hardening

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 contribution from solid solution hardening due to Mo and W to the overall creep strength of creep-resistant steels is practically superimposed on other strengthening mechanisms, eg, precipitation hardening. The addition of Mo and W sometimes causes the precipitation of Fe2(Mo,W) Laves phase and enhances fine distributions of M23C6 carbides during exposure at elevated temperature. The M in M23C6 means the metallic elements and C the carbon. European scientists and engineers have favored the addition of Mo for enhancing the solid solution hardening of 9 to 12Cr steels, while Japanese have utilized W.

Fig. 10.3 shows the amount of Fe2(Mo,W) Laves phase in 0.08C-9Cr-(W/Mo)-0.2V-0.05Nb-0.05N-0.005B steel at 650°C as a function of 1/2W/(1/2W+Mo) and also the creep rupture data for 0.08C-9Cr-(W/Mo)-0.2V-0.05Nb-0.05N-0.005B steel with 3W-0Mo and 0W-1.5Mo at 600–700°C [24]. The amount of Fe2(Mo,W) Laves
phase was estimated by Thermo-Calc. Because the atomic weight of W is two times of Mo, the atomic concentration of W in the 9Cr steel with 3W-0Mo is the same as that of Mo in the 9Cr steel with 0W–1.5Mo. The increase in the amount of Fe$_2$(Mo,W) Laves phase with increasing 1/2W/(1/2W + Mo) indicates that the concentration of dissolved W and Mo in the matrix decreases with increasing 1/2W/(1/2W + Mo). The higher creep rupture strength of the 9Cr steel with 3W-0Mo than the 9Cr steel with 0W–1.5Mo shown in Fig. 10.3(b) indicates that the solid solution hardening due to W and Mo is not a main strengthening mechanism for the 9Cr steel. The addition of W stabilizes fine distributions of M$_{23}$C$_6$ carbides in the 9Cr steel during creep,
enhancing the precipitation hardening due to $M_{23}C_6$ carbides. Although the precipitates of Fe$_2$(Mo,W) Laves phase are prone to coarsening in 9Cr steels during creep at 600–650°C, the precipitation hardening and boundary hardening enhanced by fine $M_{23}C_6$ carbides are the main strengthening mechanisms for the 9Cr steel.

Regarding the effect of interstitial solute atoms, it is proven that nitrogen is beneficial to the long-term creep strength of ferritic and austenitic creep-resistant steels through its solid solution hardening as well as precipitate hardening by forming fine nitrides.

10.3.2 Precipitation hardening

To achieve enough strengthening by this effect, creep-resistant steels usually contain several kinds of carbides, carbonitrides, intermetallic compounds, and metallic phases in the matrix and at grain boundaries (GBs). The common carbides and carbonitrides in steels are $M_{23}C_6$, $M_6C$, $M_7C_3$, MX, and $M_2X$. The X in MX and $M_2X$ means the carbon and nitrogen. Intermetallic compounds mainly consist of Fe$_2$(Mo,W) Laves phase, Fe$_7$W$_6$-$\mu$ phase, $\chi$ phase, and so on.

Several mechanisms have been proposed for the threshold stress, which is defined as the stress needed for a dislocation to pass through precipitate particles, such as the Orowan mechanism, local climb mechanism, general climb mechanism, and Srolovitz mechanism [25]. The Orowan stress $\sigma_{or}$ is given by

$$\sigma_{or} = 0.8 \frac{MGb}{\lambda}$$  \hspace{1cm} (10.1)

where $M$ is the Taylor factor (= 3), $G$ the shear modulus, $b$ the magnitude of the Burgers vector, and $\lambda$ is the mean interparticle spacing [21]. Typical values of the volume fraction, diameter, and spacing of the major particles contained in martensitic 9 to 12Cr steels after tempering are listed in Table 10.1, together with the Orowan stress estimated from the values of interparticle spacing [21].

The coarsening of fine precipitates, such as $M_{23}C_6$, MX, and Fe$_2$(W,Mo) Laves phase, and the dissolution of fine MX to form massive precipitates of $Z$ phase, which have been observed in 9 to 12Cr steels, increase the $\lambda$ term in Eq. (10.1) and hence decrease the Orowan stress. This results in a drastic reduction in the resistance to creep and causes a premature creep rupture.

<table>
<thead>
<tr>
<th>Particle</th>
<th>Volume fraction $V$ (%)</th>
<th>Diameter $d_p$ (nm)</th>
<th>Spacing $\lambda_p$ (nm)</th>
<th>Orowan stress $\sigma_{or}$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_2$(W,Mo)</td>
<td>1.5</td>
<td>70</td>
<td>410</td>
<td>95</td>
</tr>
<tr>
<td>$M_{23}C_6$</td>
<td>2</td>
<td>50</td>
<td>260</td>
<td>150</td>
</tr>
<tr>
<td>MX</td>
<td>0.2</td>
<td>20</td>
<td>320</td>
<td>120</td>
</tr>
</tbody>
</table>

Table 10.1 Volume fraction, diameter and spacing of each kind of precipitates in martensitic 9 to 12Cr steels, together with Orowan stress estimated from the values of interparticle spacing
Sawada and coworkers observed that the number density of Z phase gradually increased with time after about 10,000 h in Gr.91 during creep at 600°C, while that of MX decreased substantially after 30,000 h, as shown in Fig. 10.4 [26]. This suggests that the MX particles become dissolved with time in favor of the growth of the thermodynamically more stable Z phase.

### 10.3.3 Dislocation hardening

For a moving dislocation, other dislocations act as obstacles. This is the most basic definition of dislocation hardening. The dislocation hardening is given by

\[
\sigma_p = 0.5 \, M G b \rho_f^{1/2},
\]  

where \( \rho_f \) is the free dislocation density in the matrix [21]. The dislocation hardening is an important strengthening mechanism in steel at ambient temperature. Martensitic 9 to 12Cr steels usually contain a high density of dislocations even after tempering, in the range of 1 to \( 10 \times 10^{14}/m^2 \) in the matrix.

In contrast, at elevated temperatures, cold working enhances softening by promoting the recovery of excess dislocations and recrystallization of the deformed microstructure, reducing the creep strength. Thus dislocation hardening is not beneficial to the long-term creep strength at elevated temperature where recovery and recrystallization take place.

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![Figure 10.4](image.png)  
*Figure 10.4 Change in number density of MX and Z phase particles in Gr.91 during creep at 600°C and 70MPa.*
10.3.4 **Boundary and sub-boundary hardening**

The tempered martensitic microstructure of 9 to 12Cr steels consists of laths, blocks, and packets in prior austenite grains after appropriate tempering, as shown schematically in Fig. 10.5. The laths, blocks, and packets have a high dislocation density with fine precipitates of $\text{M}_{23}\text{C}_6$ mainly along various boundaries as well as fine MX mainly in the matrix. The $\text{M}_{23}\text{C}_6$ carbides are usually rich in Cr, while the MX carbonitrides are rich in V and Nb. Fig. 10.6 shows the TEM micrograph of Gr.91 (9Cr-1Mo-VNb steel) after normalizing and tempering.

The laths and blocks can be regarded as elongated subgrains. The sub-boundary hardening due to the presence of laths and blocks is given by

$$\sigma_{sg} = 10Gb/\lambda_{sg}$$  \hspace{1cm} (10.3)

where $\lambda_{sg}$ is the short width of elongated subgrains [21].

![Figure 10.5](image1.png) **Figure 10.5** Schematic illustration of tempered martensitic microstructure of 9 to 12Cr steels.

![Figure 10.6](image2.png) **Figure 10.6** TEM micrograph of Gr.91 after normalizing and tempering.
The subgrain width $\lambda_{sg}$, corresponding to the width of laths and blocks, in martensitic 9 to 12Cr steels is in the range of 0.3–0.5 $\mu$m after tempering. The values of $G=64$ GPa at 650°C, $b=0.25$ nm, and $\lambda_{sg}=0.3–0.5$ $\mu$m give the sub-boundary hardening of 530–320 MPa, which is much higher than the Orowan stress given in Table 10.1 for Fe$_2$(W, Mo), M$_{23}$C$_6$, and MX. The sub-boundary hardening enhanced by fine distributions of precipitates along boundaries gives the most important strengthening mechanism for creep of tempered martensitic 9 to 12Cr steels.

### 10.4 Degradation in creep strength at long times

The loss of creep strength at long times has extensively been investigated for a number of martensitic 9 to 12Cr steels [22,23]. The proposed mechanisms for microstructure degradation during creep exposure leading to the loss of creep strength are classified next:

1. precipitation of thermally stable phases and dissolution of fine carbonitrides
2. preferential recovery of microstructure near PAGBs
3. combined coarsening of laths and precipitates
4. recovery of excess dislocations resulting from low-temperature tempering
5. static recovery
6. adverse effect of $\delta$-ferrite
7. loss of creep ductility

It is possible to combine several mechanisms, but it is often difficult to quantify the contribution of each mechanism to the overall creep strength loss. For the development of advanced martensitic steels, which will be described in Section 10.6, we need to take the alloy design for minimization of the degradation into account. In the following, the recent topics on degradation mechanisms are described.

With respect to the effect of precipitation of thermally stable phases and dissolution of existing fine carbonitrides, European scientists and engineers have considered that the precipitation of Z phase exhibits the most detrimental effect on the creep strength of martensitic 9 to 12Cr steels. The Z phase is a complex nitride in the form of Cr(Nb,V)N. The precipitation of Z phase takes place after a long time at and above 550°C, and it forms large particles at the expense of previously existing fine vanadium nitrides, consequently leaving a vanadium nitride-free zone around the Z phase [27–29]. This causes a drastic loss of creep strength. 12Cr steels are more susceptible to the precipitation of Z phase than 9Cr steels [30]. Higher concentrations of Ni and nitrogen also accelerate the precipitation of Z phase [31,32]. It should be noted that there are some discrepancies about the experimental results concerning the effect of Z phase on the degradation in creep rupture strength of 9 to 12Cr steels. Sklenicka and coworkers pointed out that the synergetic effect of Z phase precipitation and tungsten depletion in solid solution due to Fe$_2$W Laves phase formation could be the reason for the sigmoidal shape of creep rupture data of TAF 650 steel (0.1C-0.55Mn-0.07Si-10.84Cr-0.14Mo-2.63W-2.86Co-0.55Ni-0.19V-0.06Nb-0.016N-0.019B) at 650°C [33]. Based on the results shown in Fig. 10.4, Sawada and coworkers concluded that the preferential recovery in the vicinity of PAGBs and the abrupt decrease in number...
density of MX particles due to Z phase formation contribute to the premature failure of Gr.91 at 600°C.

Di Gianfrancesco and coworkers investigated the microstructural evolution in P91 after very long-term creep testing, more than 100,000 h at 550, 600, and 650°C [34]. They observed the precipitate particles of Z phase in P91 after aging at 600 and 650°C for more than 100,000 h. Because their creep rupture data showed no degradation for more than 100,000 h, they pointed out that the Z phase could not be listed among the degradation mechanisms of Gr.91. Maruyama and coworkers investigated the microstructure evolution and degradation in creep rupture strength of Gr.91 at 600 to 700°C [35,36]. The creep rupture data exhibit the degradation in creep strength at low stresses and long times above about 10,000 and about 200 h at 650 and 700°C, respectively. Their results on the microstructure observations show no precipitation of Z phase and no disappearance of existing MX. They reported that MX precipitates and Z phase have nothing to do with the breakdown. We need further discussion about the effect of Z phase formation on the degradation in creep rupture strength and also about the main strengthening mechanisms in creep of 9 to 12Cr steels.

Al and Ti form AlN and TiN in creep-resistant steels by consuming nitrogen and fine nitrides during creep exposure because Al and Ti are strong nitride-forming elements. This leads to the degradation in creep strength. Usually, Al is used as a deoxidizing element in melting and casting process of creep-resistant steels, and hence a small amount of Al remains in the steels after casting as an impurity in the form of Al$_2$O$_3$ and soluble Al. Soluble Al can form AlN during creep exposure. Fig. 10.7 shows the degradation in creep rupture strength of a high Al heat of tempered martensitic 12Cr-1Mo-1W-0.3V steel for a turbine blade [37,38]. The creep rupture data are substantially the same between the low and high Al heats at short times, while the degradation in creep rupture strength becomes more significant in the high Al heat with increasing test duration at long times above 10,000 h at 550°C. The formation of AlN particles has been observed after long-term creep exposure. Soluble nitrogen and fine

![Figure 10.7](image-url) Effect of Al on creep rupture data for 12Cr-1Mo-1W-0.3V steel.
nitrides are available for creep strengthening but the formation of AlN and TiN during creep offsets the beneficial effect of nitrogen. Therefore, the available nitrogen concentration $N_{av}$ is defined as the concentration of nitrogen free from AlN and TiN. Assuming the formation of stoichiometric compound of AlN and TiN, the $N_{av}$ is described as

$$N_{av} = \text{Nitrogen} - \text{Al} - \text{Ti} \quad \text{(at \%)}$$

which corresponds to

$$N_{av} = \text{Nitrogen} - 0.519 \text{ Al} - 0.292 \text{ Ti} \quad \text{(mass \%)}$$

and

$$N_{av} \text{ (mass \%)} = \frac{1}{4} N_{av} \text{ (at \%)}$$

The time to rupture of the nine heats of 12Cr-1Mo-1W-0.3V steel in NIMS Creep Data Sheets decreases as the available nitrogen concentration $N_{av}$ decreases at low stresses and long times. In Gr.91, the insufficient initial strength associated with low nitrogen and high Al after tempering heat treatment results in insufficient creep strength at elevated temperature, and a high concentration of Al is more susceptible to forming cracks early in life [39]. Another topic on the effect of impurities is Ni. The results that Ni accelerates the degradation in long-term creep rupture strength of Gr.91 have been reported [40]. The EPRI guideline recommends less than 0.2% Ni for Gr.91, which is lower than the level of 0.4% currently stated in the ASME/ASTM specifications [41].

With respect to the effect of preferential recovery of microstructure near PAGBs and the effect of combined coarsening of laths and precipitates, Fig. 10.8 shows a

![Figure 10.8 Creep rupture data for 9Cr-3W-3Co-VNb steel at 650°C.](image-url)
loss of creep rupture strength for a 9Cr-3W-3Co-0.2V-0.05Nb steel with 0.08% carbon but no addition of nitrogen at long times above about 1000h at 650°C [42]. The residual nitrogen concentration of the steel was only 0.0019% (19 ppm), suggesting an extremely low amount of MX carbonitrides and hence an extremely low driving force for Z phase formation during creep. Therefore, the dissolution of fine $M_2X$ and MX carbonitrides and the precipitation of Z phase cannot be responsible for the loss of creep rupture strength. The proposed mechanism for the loss of creep strength in the steel is the coarsening of $M_{23}C_6$ carbides and laths in the vicinity of PAGBs.

Kushima and coworkers observed the preferential recovery of lath martensitic microstructure in the vicinity of PAGBs of Gr.91 after creep rupture testing for 34,141h at 600°C and 100 MPa [43]. The preferential recovery promotes localized creep deformation in the vicinity of PAGBs, which results in the premature creep rupture.

With respect to the effect of recovery of excess dislocations resulting from low-temperature tempering, excess dislocations resulting from low-temperature tempering (750°C) promote a rapid reduction in creep rupture strength in 12Cr-1Mo-1W-VNb steel at 600 and 650°C over long periods; see Fig. 10.9 [44]. This is because excess dislocations accelerate recovery and recrystallization during creep with the aid of stress, which also accelerates microstructure evolution during creep. The high-temperature tempering (800°C) results in a lower dislocation density, suggesting less driving force is available for microstructural evolution during creep. The tempering is usually carried out at temperatures of about 700°C or lower for 12Cr turbine steels, whereas it is as high as 750–800°C for 9 to 12Cr boiler steels. Therefore, the stabilization of microstructure including excess dislocations is more critical for turbine steels than for boiler steels.

With respect to the effect of static recovery, Maruyama and coworkers recently proposed that the tempered martensitic microstructure in 9 to 12Cr steels remains unchanged during short-term aging, whereas the static recovery of lath martensitic microstructure proceeds during aging when the diffusion distance is sufficiently long, as is the case in the long-term creep [35,36]. Fig. 10.10 shows the creep rupture data and Vickers

Figure 10.9 Effect of tempering temperature on creep rupture strength of 12Cr-1Mo-1W-VNb steel at 600 and 650°C.
hardness in the grip portion of the creep ruptured specimens of Gr.91. The creep rupture data exhibit the degradation in creep strength at low stresses and long times at 650 and 700°C. The hardness of Gr.91 is kept constant at short times during aging, whereas it decreases at long times due to the static recovery of lath martensitic microstructure at 650 and 700°C. The static recovery means the recovery due to thermal aging under no stress. The drop in hardness accords very well with the degradation in creep strength, suggesting that the static recovery of lath martensite microstructure causes the degradation in creep strength of Gr.91.

The subgrain width is kept constant in the time range shorter than 5000h at 650°C and 100,000h at 600°C, and then increases with increasing aging time, Fig. 10.11. The interparticle spacing of MX precipitates does not change at all, even after long-term aging, due to their high thermal stability, while that of $M_23C_6$ precipitates is kept constant up to

![Figure 10.10](image)

**Figure 10.10** (a) Creep rupture data and (b) hardness change in head portion under no stress (thermal aging) of Gr.91.
5000 h at 650°C and 100,000 h at 600°C, and then it increases with increasing aging time. Maruyama and coworkers consider that subgrain boundaries are the major obstacles to dislocation motion in 9 to 12Cr steels, and the creep strength of Gr.91 is determined by subgrain width [21]. There are two types of recovery processes of subgrains that happen in Gr.91 steel during creep exposure: strain-induced recovery and static or thermal recovery. Since the static recovery of subgrains happens during long-term creep, the acceleration of creep deformation and the consequent breakdown of creep strength should take place in this region. The static recovery of subgrains is caused by a loss of pinning force from M$_{23}$C$_6$ precipitates due to coarsening.

With respect to the adverse effect of δ-ferrite, the degradation in creep strength of dual-phase 12Cr steel (12Cr-0.4Mo-2W-CuVNb steel, specified as KA-SUS410J-3DTB) is explained by this effect [45,46].
With respect to the effect of loss of creep ductility, Maruyama and coworkers pointed out that the loss of ductility is the origin of the loss of creep rupture strength in 11Cr-2W-0.3Mo-CuVNb steel at 650°C [21].

10.5 Fundamental aspects of tempered martensitic microstructure and creep deformation

The tempered martensitic microstructure of creep strength–enhanced ferritic steels, such as Gr.91 (9Cr-1Mo-VNb steel), Gr.92 (9Cr-0.5Mo-1.8W-VNb steel), and Gr.122 (11Cr-0.4Mo-2W-CuVNb steel), consists of laths, blocks, and packets in prior austenite grains. The coarsening rate of $M_23C_6$ carbides is much larger in the vicinity of PAGBs than within grain. The stabilization of fine precipitates, especially at and near PAGBs, for up to long times is a key issue for the suppression of creep strength loss, as will be described later.

The creep and creep rate curves consist of the primary or transient creep region, where the creep rate decreases with time, and of the tertiary or acceleration creep region, where the creep rate increases with time after reaching a minimum creep rate, as shown schematically in Fig. 10.12. There is substantially no steady-state region, where the creep rate is constant. In tempered martensitic steels, there is an ever evolving microstructure, and the change in creep rate reflects coupled elementary processes, such as micro-grain growth, change in dislocation density, and change in precipitate volume fraction and size [47,48]. This suggests that there is no dynamic microstructural equilibrium in tempered martensitic steels during creep. During creep, the recovery of excess dislocations and the coarsening of precipitates and laths take place with the aid of stress and strain.

The present author has revealed for tempered martensitic 9Cr steel that the transient creep is basically a consequence of the movement and annihilation of a high density of dislocations produced by martensitic transformation during cooling after normalizing and also produced by plastic deformation upon loading and that the acceleration creep is a consequence of gradual loss of creep strength due to the microstructure evolution [47,48]. He has also suggested that the migration of lath or block boundaries, causing the coarsening of the laths or blocks in the acceleration creep region, is closely correlated with the onset of acceleration creep. The creep life $t_r$ of Gr.91 is correlated with the onset time of acceleration creep, namely, the time to minimum creep rate $t_m$ as [49,50].

$$t_r = g t_m.$$ (10.7)

$$\frac{1}{g} = \left( \frac{t_m}{t_r} \right)$$

$$= 1.10 \times 10^{-1} \log \sigma + 2.90 \times 10^{-3} \quad \text{at 40 to 100 MPa}$$

$$= 4.05 \times 10^{-1} \log \sigma - 5.89 \times 10^{-1} \quad \text{at 100 to 260 MPa}$$ (10.8)

The ratio of the time to minimum creep rate to the creep life ($t_m/t_r$) slightly decreases with decreasing stress: $t_r = 4.5 t_m$ at 100 MPa. The average value of $g$ over a wide temperature and stress range is evaluated to be 3.7.
The coarsening rate of precipitates during creep is much larger at and in the vicinity of PAGBs than within grain because of enhanced diffusion along PAGBs. The coarsening of precipitates increases the interparticle distance and reduces the pinning of boundaries for migration. This suggests that the stabilization of fine precipitates, especially at and near PAGBs, for up to long times is a key issue for the suppression of boundary migration, which results in the retardation of onset of acceleration creep.

10.6 New martensitic 9Cr steel

10.6.1 Precipitate design

Bhadeshia pointed out that in a multiphase system such as creep-resistant 9 to 12Cr steels, the coarsening behavior of precipitates is greatly influenced by the presence of other phases [51]. In the following, for simplicity, we will describe what kind of precipitate phases are the most appropriate as coarsening-resistant phases during
New martensitic steels exposure at elevated temperature, based on Fe-M-C alloys, where M is alloy element and C is carbon [9]. The volume diffusion controlled Ostwald ripening of \( M_a C_b \) carbides in Fe-M-C alloys has been given by the following [52].

\[
\begin{align*}
    r^3 - r_0^3 &= k_3 t \\ 
    k_3 &= 8 (a + b) \sigma V D_M u_M / 9 a R T (u_p M - u_M)^2
\end{align*}
\]

where \( r \) and \( r_0 \) are the average particle radius at the time \( t \) 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 \( u_p M \) are the concentration of \( M \) in matrix and carbides, respectively, \( R \) is gas constant, and \( T \) is temperature. The main factors affecting the coarsening rate of precipitate particles are diffusion coefficient, solid solubility of participating elements, and interfacial energy. We evaluate the diffusion coefficient and solid solubility of alloying elements in iron. Impurity diffusion coefficients in iron are not so different, less than one order of magnitude, among different elements, such as W, Mo, V, and Nb [53]. On the other hand, the solid solubility of alloying elements, which are equilibrating with their carbides, nitrides, and \( Fe_2(Mo,W) \) Laves phase in Fe-M-0.1%C ternary, Fe-M-0.05%N ternary, and Fe-M binary alloys, respectively, is evaluated by using Thermo-calc. This is shown in Fig. 10.13. The solid solubility of V, Nb, and Ti equilibrating with their nitrides in Fe-M-0.05% N alloys is very low. It should be noted that TiN is extremely stable for up to melting temperature because of extremely low solid solubility in iron for up to melting temperature. This indicates that we cannot control a dispersion of fine TiN by appropriate heat treatment, such as solution treatment and subsequent aging or tempering. Thus TiN is excluded from the present precipitate designing. Carbides and nitrides of V and Nb and carbides of Ti are the most appropriate candidates, which show very low coarsening rate during exposure at elevated temperature. However, the addition of carbon to a 9Cr steel causes the formation of a large amount of \( M_{23}C_6 \) carbides rich in Cr. Wey and co-workers reported that the coarsening rate of Cr carbides in iron was much larger than that of V and Nb carbides at elevated temperature [52]. Therefore, it is crucial for 9Cr steel to reduce carbon concentration to very low amounts, so as to promote the formation of MX nitrides as very fine and thermally stable particles for prolonged periods of exposure at elevated temperatures and also to eliminate unstable Cr-rich carbides \( M_{23}C_6 \) [54,55].

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 Fig. 10.14 as a function of carbon concentration. Three kinds of precipitate phases of \( M_{23}C_6 \) carbide, MX carbonitride, and \( Fe_2W \) Laves phase appear as equilibrium precipitate phases at 800°C. However, \( Fe_2W \) Laves phase does not precipitate in the present steel during tempering at 800°C for 1 h, because of short tempering time. Therefore, \( Fe_2W \) Laves phase is neglected in Fig. 10.14. The change in amount of \( M_{23}C_6 \) and MX with carbon concentration at a creep test temperature of 650°C is similar as those at 800°C. The amount of \( M_{23}C_6 \) carbides rich in Cr decreases with decreasing carbon concentration, while the amount of MX carbonitrides is approximately constant for a wide range of carbon
Figure 10.13  Solid solubility of alloying elements, which are in equilibrium with their carbides, nitrides and the Fe$_2$(Mo, W) Laves phase in iron.

Figure 10.14  Amounts of M$_{23}$C$_6$ carbides and MX carbonitrides in 9Cr-3W-3Co-0.2V-0.05Nb-0.05N steel at tempering temperature of 800°C as a function of carbon concentration.
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concentration from 0% to 0.15%. The amount of MX carbonitrides is larger than that of \( M_{23}C_6 \) carbides at low-carbon concentrations below 0.02%. The MX carbonitrides consist of mainly vanadium nitrides and of small amount of niobium carbides, suggesting that the MX carbonitrides are substantially vanadium nitrides. This indicates that we can obtain substantially vanadium nitrides alone after tempering by reducing carbon concentration to very low amounts below 0.02%.

In the present research, a fine dispersion of thermally stable precipitates against coarsening and its effect on creep strength have been examined for a tempered martensitic 9Cr steel on the basis of following scenarios:

1. elimination of unstable \( M_{23}C_6 \) carbides and dispersion of nano-size MX carbonitrides alone by reducing carbon concentration
2. reduction of coarsening rate of \( M_{23}C_6 \) carbides near PAGBs by using boron
3. combination of coarsening-resistant \( M_{23}C_6 \) carbides and nano-size MX carbonitrides

### 10.6.2 Martensitic 9Cr steel strengthened by nanometer-size MX nitrides: MARN

Based on the estimation in Fig. 10.14, elimination of unstable \( M_{23}C_6 \) carbides and dispersion of nanometer-size MX nitrides were examined using 9Cr-3W-3Co-0.2V-0.05Nb-0.05N steel with different carbon concentrations of 0.002, 0.018, 0.047, 0.078, 0.120, and 0.160% [54,55]. A large number of fine precipitate particles having a size less than 10 nm are distributed along boundaries, such as PAGBs and lath, block, and packet boundaries, and in the matrix of the steel with 0.002% C after tempering, as shown in Fig. 10.15. This is quite different from the microstructure of the steel with 0.078% C, where the large particles of \( M_{23}C_6 \) carbides of 100–300 nm size are distributed along PAGBs together with the fine particles of MX carbonitrides.

The time to rupture is substantially independent of carbon concentration in the higher carbon region above 0.047%, but it significantly increases in the lower carbon region below 0.018%, as shown in Fig. 10.16, which is also typical for applied stresses within the range of 140–200 MPa. On the other hand, the minimum creep rate significantly decreases in the lower carbon region below 0.018%. It is evident that the creep strength of 9Cr steel significantly improves by the elimination of \( M_{23}C_6 \) carbides and a dispersion of nanometer-size MX nitrides alone.

Fig. 10.17 compares the creep rate versus time curves between the two representative steels in Fig. 10.16 with 0.002% and 0.078% C at 650°C and 140 MPa [56]. 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 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 of the steel with 0.078% carbon. The observed longer creep life by reducing carbon concentration results from a decrease in minimum creep rate. The lower values of the initial creep rates in the steel with 0.002% carbon than in the steel with 0.078% carbon results from larger precipitation hardening after tempering. However, the difference in initial creep rates between the two steels is only slight as shown by 1/3 orders of magnitude, which is much smaller than the difference
in minimum creep rate between the two steels. On the other hand, the onset of acceleration creep is retarded up to longer times in the steel with 0.002% carbon, which further decreases the minimum creep rate. The present very low-carbon 9Cr steel is designated MARN (MARtensitic 9Cr steel strengthened by nano-size MX nitrides).

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 earlier, the density of MX carbonitrides in the matrix within laths is lower in the steel with 0.002% carbon than
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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 [55,56]. This is due to the amount of MX carbonitrides along boundaries being much larger in the steel with 0.002% carbon than in the steel with 0.078% carbon because of no $M_{23}C_6$ carbide in the steel with 0.002% carbon. On the other hand, most of MX carbonitrides in the steel with 0.078% carbon are distributed in the matrix, and only a slight amount of MX carbonitrides is distributed along boundaries together with large amount of $M_{23}C_6$ carbides. The fine MX carbonitrides in the matrix act as obstacles for dislocation movement to lath and block boundaries, which reduces the dislocation annihilation and decreases the creep rate, as illustrated in Fig. 10.18. At lath and block boundaries, 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 reduces the efficiency of dislocation absorption at boundaries. This also reduces dislocation annihilation and decreases the creep rate. Therefore, the creep rate in the transient region is given by the following [9,56]:

$$\dot{\varepsilon} = \rho_f v_g b \eta,$$

(10.11)

where $\rho_f$ is the free dislocation density in the matrix within laths, $v_g$ is the velocity of free dislocations in the matrix, $b$ is the magnitude of Burgers vector, and $\eta$ is the efficiency of dislocation absorption at boundaries. The 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 along boundaries is a main factor for the lower creep rate in the transient region rather than the precipitation hardening due to fine MX in the matrix. The agglomeration and coarsening of precipitates at boundaries during transient creep promote climbing and redistribution of dislocations in the boundary wall, resulting in an increase of the

Figure 10.17 Creep rate versus time curves of 9Cr-3W-3Co-0.2V-0.05Nb-0.05N steel with 0.002% and 0.078% C at 650°C and 140 MPa.
efficiency of dislocation absorption at boundaries. The absorption of dislocations at boundaries accelerates further agglomeration and coarsening of precipitates and also promotes climbing and redistribution of dislocations in the boundary wall. These chain reactions promote the migration of lath or block boundaries, promoting the onset of acceleration creep. The present results suggest that the boundary and sub-boundary hardening enhanced by fine distributions of precipitates along lath and block boundaries is a main strengthening mechanism for creep of the present 9Cr steel.

10.6.3 Martensitic 9Cr steel strengthened by boron and MX nitrides: MARBN

10.6.3.1 Effect of boron

Fig. 10.19 shows the creep rupture data for 9Cr-3W-3Co-0.2V-0.05Nb steel with different boron concentrations (0, 48, 92, and 139 ppm B) at 650°C. Nitrogen was not added in the steel to avoid the formation of boron nitrides (BN) [57]. The base steel without boron (0 ppm B) exhibits a loss of creep rupture strength at long times above about 1000 h at 650°C. With increasing boron concentration, however, the time to rupture significantly increases at low stress and long time conditions. The long-term creep rupture strength of T/P92 (9Cr-0.5Mo-1.8W-VNb) [58] is roughly the same as the present 9Cr steel with 92 ppm boron, while that of T91 (9Cr-1Mo-VNb) [59] is roughly the same as the present 9Cr steel with 48 ppm boron. The long-term creep rupture strength of P122 (11Cr-0.4Mo-2W-1Cu-VNb) [60] is located at intermediate between that of T91 and T/P92.

The addition of boron also improves the creep rupture ductility at 650°C and long times as shown in Fig. 10.20 for the reduction of area, although the reduction of area is roughly the same among the steels containing 48–139 ppm boron. This suggests that the localization of creep deformation near PAGBs is less pronounced by the addition

![Figure 10.18 Schematics of dislocation movement in lath and block microstructure of 9Cr steel. (a) 0.002% C–0.05% N and (b) 0.078% C–0.05% N.](image)
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of boron. The reduction of area after long-term creep rupture testing is on order of 9Cr-boron steel $\geq$ T91 $>$ T/P92. The improved reduction of area by the addition of boron is advantageous to the creep-fatigue life because the creep-fatigue life is proportional to the reduction of area in creep rupture test, namely, proportional to the creep ductility but not proportional to the creep strength [61].

The fine distribution of $M_23C_6$ carbides along PAGBs is maintained in the 9Cr steel with 139 ppm boron during exposure at 650°C, Fig. 10.21 [62]. The analysis
by means of field emission type auger electron spectroscopy (FE-AES) shows that boron is enriched in M$_{23}$C$_6$ carbides, which is more significant at and near PAGBs than inside the grains, suggesting GB segregation of boron. This is correlated with the reduction of coarsening rate of M$_{23}$C$_6$ carbides in the vicinity of PAGBs. 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 exposure at 650°C.

The onset of acceleration creep is retarded and the transient creep region continues for up to a longer time with increasing boron concentration, Fig. 10.22. The longer duration of the transient creep region, which corresponds to a larger value of $t_m$ in Eq. (10.7), results in a lower minimum creep rate and a longer time to rupture. The extensive coarsening of M$_{23}$C$_6$ carbides in the vicinity of PAGBs in the base steel without boron promotes the migration of lath and block boundaries during creep, and hence the onset of acceleration creep takes place at earlier times, resulting in higher minimum creep rate and shorter time to rupture. The boundary and sub-boundary hardening enhanced by the distributions of M$_{23}$C$_6$ carbides along boundaries is the most important strengthening mechanism for long-term creep.

10.6.3.2 Additive strengthening due to boron and MX nitrides

The nitrogen concentration dependence of the time to rupture and minimum creep rate of 9Cr-3W-3Co-0.2V-0.05Nb steel containing about 140 ppm boron at 650°C and 120 MPa is shown in Fig. 10.23(a) [63]. The peaks of the time to rupture and
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minimum creep rate are located at about 80 to 100 ppm nitrogen, which corresponds to the maximum solid solubility of nitrogen in equilibrium with BN in the steel containing 140 ppm boron at a normalizing temperature of 1100°C; see Fig. 10.23(b) [64]. This indicates that the addition of nitrogen without the formation of any BN during normalizing significantly improves the creep strength, but excess addition of boron and nitrogen causes the formation of BN during normalizing heat treatment, which consumes soluble boron and nitrogen and degrades the creep strength.

Excess addition of boron and nitrogen also degrades the creep rupture ductility at 650°C and long times, as shown in Fig. 10.24. The degradation in reduction of area is significant in the present steels containing 300 and 650 ppm nitrogen, where a large amount of BN is formed during normalizing. The present results suggest that BN formed during normalizing provides preferential nucleation sites for creep voids. On

Figure 10.22 (a) Effect of boron on creep rate versus time curves of the steels at 650°C and 80 MPa and (b) mechanisms of boron effect on creep rate versus time curves.

Figure 10.23 (a) Time to rupture and minimum creep rate of 9Cr steel with 140 ppm boron at 650°C and (b) composition diagram of boron and nitrogen at a normalizing temperature of 1050–1150°C.
the other hand, the present steel containing nitrogen less than 100 ppm exhibits enough reduction of area, larger than or the same as T91.

Inclusions in 9 to 12Cr steels were examined by SEM observations of ductile fracture surface combined with energy dispersive X-ray spectrometry (EDS) analysis [63]. In ductile fracture of steels, inclusions provide nucleation sites for microvoids, which grow and coalesce as the strain increases, exhibiting a dimple pattern. The SEM observations of ductile fracture surface enable us to characterize inclusions more effectively than the conventional method of optical microscopic observations of polished cross-section. Although the EDS analysis is less sensitive to light elements such as boron than the FE-AES and secondary ion mass spectrometry (SIMS), the EDS analysis can easily characterize BN inclusions because of their large size of several μm or more.

Rod specimens, having a size of 3.6 mm diameter and 50 mm length with a 0.8 mm depth circular notch at the center of rod, were bent and fractured at room temperature. Fig. 10.25 shows an example of the characterization of boron nitride particles in 9Cr-3W-3Co-0.2V-0.05Nb steel with 71 ppm boron and 480 ppm nitrogen in as tempered [65]. A large number of boron nitride inclusions were observed at the bottom of dimples on the ductile fracture surface, together with Al₂O₃ inclusions. Gu and coworkers made analysis of the creep voids formed in P92 steel after creep exposure [66]. Their analysis revealed that the majority of creep voids were associated with hard inclusions. Chemical analysis of these inclusions showed that the vast majority were BN, although some Al₂O₃ and MnS particles were also observed.

Based on the characterization of boron nitride inclusions, the solubility product for boron nitride in 9 to 12Cr steels at a normalizing temperature of 1050–1150°C is given by [65]

\[
\log [\text{B}] = -2.45 \log [\text{N}] - 6.81,
\]
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where \( [\%B] \) and \( [\%N] \) are the concentration of soluble boron and soluble nitrogen in mass \%, respectively [14]. This is shown in Fig. 10.23(b). At a boron concentration of 140 ppm in 9Cr steel, only 95 ppm nitrogen can dissolve in the matrix. On the other hand, at a nitrogen concentration of 0.05\% (500 ppm), which corresponds to the nitrogen concentration in Gr.91, Gr.92, and Gr.122, the maximum soluble boron concentration is only 3 ppm.

The formation of BN consumes soluble boron. Fig. 10.26 compares the enrichment of boron in \( M_{23}C_6 \) carbides between 9Cr-3W-3Co-VNb steel with 0.0015 and 0.065N [63]. FE-AES was used for analyzing boron. In the 0.0015N steel, no boron nitride forms during normalizing heat treatment, and hence most of boron can contribute to the GB segregation and to the enrichment in \( M_{23}C_6 \) carbides near PAGBs. On the other hand, in the 0.065N steel, a large amount of BN forms during normalizing at high temperature. Therefore, most of boron is consumed to form the BN. 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 concentration.

SIMS is another potential technique for analyzing light elements such as boron. Two different types of SIMS equipment were used for analyzing boron: dynamic SIMS with a quadrupole-type mass analyzer and time-of-flight (ToF) type SIMS employing a micro-focused ion beam [67]. 9Cr-3W-3Co-0.2V-0.05Nb steel with 47B-17N, 130B-71N and 150B-300N (ppm) in as tempered were used for the SIMS analysis.

**Figure 10.25** SEM micrograph of ductile fracture surface of 9 Cr-3W-3Co-0.2V-0.05Nb steel with 71 ppm B and 480 ppm N and EDS analysis of inclusions.
The secondary negative ions of \( \text{BO}^2- \) were used to analyze the distribution of boron in the specimen. This is shown in Fig. 10.27. Boron is enriched along PAGBs, at which \( \text{M}_{23}\text{C}_6 \) carbides are distributed, in the 9Cr steel with 47B-17N and 130B-71N (ppm), while relatively large particles containing boron form in the matrix but no enrichment of boron along PAGBs in the 9Cr steel with 150B-300N (ppm).

Because the ion images obtained by ToF-SIMS shown in Fig. 10.27 are less quantitative, line scans of the secondary ion counts of \( \text{BO}^2- \) were carried out, together with \( \text{CN}^- \), \( \text{CrO}_3^- \), and \( \text{FeO}_2^- \) ions. This is shown in Fig. 10.28, which shows the line scan of \( \text{BO}^2- \), \( \text{CN}^- \), \( \text{CrO}_3^- \), and \( \text{FeO}_2^- \) ions in 9Cr steel with 47B-17N, 130B-71N, and 150B-300N (ppm) by ToF-SIMS. The correlative distribution of \( \text{BO}^2- \) and \( \text{CrO}_3^- \) ions in the 9Cr steel with 47B-17N and 130B-71N (ppm) suggests the enrichment of boron in \( \text{M}_{23}\text{C}_6 \) carbides rich in Cr, which corresponds to the enrichment of boron along PAGBs shown in Fig. 10.27. The correlative distribution of \( \text{BO}^2- \) and \( \text{CN}^- \) ions in the 9Cr steel with 150B-300N (ppm) shows the formation of boron nitride particles, which corresponds to relatively large particles containing boron in Fig. 10.27. It should be noted that the formation of BN consumes most of the boron in the specimen, resulting in a lower concentration of boron in the matrix.

Figure 10.26 Concentration of boron in \( \text{M}_{23}\text{C}_6 \) carbides in the steels after creep rupture testing at 650°C for 3000–4000h, as a function of distance from prior austenite grain boundary.

Figure 10.27 Imaging of \( \text{BO}^2- \) ions in 9Cr steel with (a) 47B-17N, (b) 130B-71N and (c) 150B-300N (ppm), by ToF-SIMS.
in no enrichment of boron along PAGBs. The results by SIMS are basically the same as those by FE-AES.

Liu and coworkers carried out the analysis of boron in 9 to 12Cr steels by means of atom probe-field ion microscopy (AP-FIM) [68]. Their results show that boron is enriched and evenly distributed inside $\text{M}_{23}\text{C}_6$ carbides but no segregation at the $\text{M}_{23}\text{C}_6$ carbide/alloy matrix interface. Their results also indicate that the enrichment of boron in $\text{M}_{23}\text{C}_6$ carbides is more significant near PAGBs, which is the same as the analysis by FE-AES shown in Fig. 10.26.

### 10.6.3.3 Suppression of Type IV fracture in HAZ of welded joints

Fig. 10.29 compares the creep rupture data between the base metals and welded joints for 9Cr-boron steel containing different boron and nitrogen concentrations and conventional steels of P92 and P122 at 650°C [42,69]. The addition of boron and nitrogen without any formation of BN during normalizing causes no grain refinement and no Type IV fracture in the heat-affected zone (HAZ) of welded joints, while the formation of BN during normalizing produces the fine-grained microstructure in HAZ and causes the premature rupture in welded joints due to Type IV fracture; see P92 and P122. Soluble boron is essential for the suppression of grain refinement and Type IV fracture.

P91, P92, and P122 contain the nitrogen of 0.05–0.06%. We observed that the addition of 0.05–0.06% nitrogen to 9Cr steel produces the fine-grained microstructure during heating of welding, irrespective of boron concentration in the range of 0–130 ppm [70].

The multiaxial stress condition in the HAZ with lower creep strength, which results from mechanical constraint effect by the surrounding weld metal and base metal with higher creep strength, is essential for the brittle Type IV fracture in the HAZ of welded joints, as shown schematically in Fig. 10.30 [71]. Using simulated HAZ specimens, we have investigated the relationship between the creep strength and microstructure
of HAZ for Gr.92 and 9Cr-3W-3Co-VNb steel with 90ppm boron (9Cr-90ppm B steel) [72]. Fig. 10.31 shows the time to rupture of the simulated HAZ specimens of Gr.92 and the 9Cr-90ppm B steel at 650°C and 110MPa, as a function of peak temperature in the thermal cycle. The thermal cycle conditions for the preparation of simulated-HAZ specimens are shown in Fig. 10.32. At a heating rate of 100K/s, the $A_{C1}$ temperature was found to be 817°C (1090 K) and 841°C (1114 K) for P92 and the 9Cr-90ppm B steel, respectively, while the $A_{C3}$ temperature was 912°C (1185 K) and 920°C (1193 K) for P92 and the 9Cr-90ppm B steel, respectively. The specimens were kept for 0.5 s at various peak temperatures between 810 and 1125°C and then cooled
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Figure 10.30 Schematics of welded joints of 9 to 12Cr steels.

Figure 10.31 Time to rupture of simulated-HAZ specimens of Gr.92 and 9Cr-90 ppm boron steel at 650°C and 110 MPa.

Figure 10.32 Thermal cycle conditions of simulated-HAZ specimens.
to room temperature. Finally, the post-weld heat treatment (PWHT) was carried out for each specimen including the base metal at 740°C for 4.7 h. The heat treatment conditions, grain size, and precipitates at GBs after PWHT in the A_C3 simulated HAZ specimens are given in Table 10.2.

The degradation in time to rupture in the A_C3 simulated HAZ specimens of Gr.92 in Fig. 10.31 shows that it is not caused by the grain refinement but that the reduction of boundary and sub-boundary hardening is the most important [72]. The A_C3 simulated HAZ specimens of Gr.92 exhibit the fine-grained microstructure, where very few M_{23}C_{6} carbides are formed along PAGBs, as shown in Fig. 10.33. Inside the grains, the A_C3 simulated HAZ specimens of Gr.92 consisted of equiaxed subgrains with low density of dislocations and sparse distributions of large M_{23}C_{6} carbides. These observations suggest that the boundary and sub-boundary hardening is significantly reduced in the A_C3 simulated HAZ specimens of Gr.92 compared with that in the base metal.

### Table 10.2 Heat treatment conditions, grain size and precipitates at GBs after PWHT in A_C3 simulated-HAZ specimens of Gr.92 and 9Cr-90 ppm B steel

<table>
<thead>
<tr>
<th></th>
<th>Heat treatment</th>
<th>Grain size after PWHT</th>
<th>Precipitates at GBs after PWHT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gr.92</td>
<td>Normalizing → Tempering → Thermal cycle → PWHT</td>
<td>fine grains</td>
<td>poor M_{23}C_{6} at PAGBs</td>
</tr>
<tr>
<td>9Cr-90B</td>
<td>Normalizing → Tempering → Thermal cycle → PWHT</td>
<td>Basically coarse grains with fine grains along GBs of coarse grains</td>
<td>Enough M_{23}C_{6} at PAGBs of coarse grains and Fe_{7}W_{6} µ phase at GBs of fine grains</td>
</tr>
</tbody>
</table>

Thermal cycle: Peak Temp. 950°C, PWHT: 740°C × 4.7 h.

Figure 10.33 (a) Optical and (b) scanning electron micrographs of Gr.92 after thermal cycle to a peak temperature of 950°C followed by PWHT.
The 9Cr-90 ppm B steel basically consists of coarse grains of roughly 200–300 μm after the A_C3 thermal cycle, which is substantially the same as that of base metal and of fine grains of 10–50 μm at PAGBs of coarse grains as shown in Fig. 10.34 [73,74]. PAGBs of the coarse grains are covered by enough M_{23}C_6 carbides even after the A_C3 thermal cycle followed by PWHT, substantially the same as the base metal. It should be noted that a large number of Fe_7W_6-μ phase forms at GBs of the fine grains during PWHT, Fig. 10.34(c). Inside the grains, the tempered martensitic microstructure substantially consists of blocks, Fig. 10.34(d). Therefore, the boundary and sub-boundary hardening is enough in the 9Cr-90 ppm B steel even after the A_C3 thermal cycle followed by PWHT, suggesting no reduction of creep strength in the A_C3-HAZ. Indeed, the time to rupture of A_C3 simulated HAZ specimens of 9Cr-90 ppm B steel is substantially the same as that of base metal as shown in Fig. 10.31.

The grain refinement behavior in Gr.92 and no grain refinement behavior in the 9Cr-boron steel during heating are explained as follows [42]. Fig. 10.35 shows schematically the microstructure evolution in these steels during thermal cycle followed by PWHT [75]. In Gr.92, the nucleation of γ phase takes place at PAGBs at temperature above A_C1 during heating, Fig. 10.35(a). This is an initial stage of diffusive α/γ transformation. The diffusive transformation produces fine-grained microstructure when the peak temperature is not so high, at around A_C3 temperature, Fig. 10.35(b). In the

![Figure 10.34](image-url) - Optical micrographs of (a) base metal and (b) simulated-HAZ specimen of 9Cr-3W-3Co-VNb steel with 90 ppm boron after thermal cycle to a peak temperature of 950°C and subsequent PWHT, (c) Fe_7W_6-μ phase precipitates at grain boundaries of fine grains and (d) TEM microstructure inside coarse grain.
9Cr-boron steel, on the other hand, the GB segregation of boron reduces GB energy and makes the GBs less effective as heterogeneous nucleation sites for \( \gamma \) phase. This retards diffusive \( \alpha/\gamma \) transformation, and hence martensitic reverse transformation by shear can take place during heating, Fig. 10.35(d). The observed higher \( A_{C1} \) temperature of 841°C for the 9Cr-90 ppm B steel at a heating rate of 100 K/s, in comparison with that of 817°C for Gr.92, is correlated with the retardation of \( \alpha/\gamma \) transformation. The nucleation of \( \gamma \) phase by diffusive transformation also take place at part of PAGBs in 9Cr-boron steel during heating, which produces the fine grains at part of PAGBs of coarse grains, Fig. 10.34(b).

Santella and coworkers performed synchrotron diffraction experiments to examine the real-time transformation behavior of the 9Cr-boron steel containing 130 ppm boron and P92 under simulated HAZ thermal cycle [76]. They showed that when heated to peak temperatures near 1100°C both steels rapidly transformed from \( \alpha \) to 100% \( \gamma \), which corresponds to the \( \alpha/\gamma \) transformation during heating of normalizing. When the 9Cr-boron steel and P92 were heated to peak temperature of 911 and 896°C, respectively, about 56% and 15% of the original \( \alpha \) never transformed to \( \gamma \) in the 9Cr-boron steel and P92, respectively, as shown in Fig. 10.36. Their results suggest the retardation of \( \alpha/\gamma \) transformation in the 9Cr-boron steel during heating in comparison with P92. Kobayashi and coworkers observed a similar effect using electric resistivity measurements to follow the \( \alpha \) to \( \gamma \) transformation in Fe-0.1C steel.

**Figure 10.35** Schematics of microstructure evolution in Gr.92 and 9Cr-boron steel during simulated-HAZ thermal cycle.
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with and without 98 ppm boron during continuous heating at a rate of 10°C/min [77]. Their results showed that the boron addition shifted the \( \alpha \) to \( \gamma \) transformation to higher temperature. Azuma and coworkers observed metallographically that the addition of 90 ppm boron retarded the transformation in 12Cr turbine steels [78].

The direct or in situ observation of the surface of 9Cr-130 ppm boron steel by using a confocal scanning laser microscope during heating clearly shows a high surface relief at a temperature of 950°C just above \( A_{C3} \), Fig. 10.37, suggesting martensitic or displacive transformation [79]. In Fig. 10.35(b), carbonitrides such as \( M_{23}C_6 \) also become dissolved during heating but cannot dissolve completely when the peak temperature is not so high, at around \( A_{C3} \). In the 9Cr-boron steel,

![Figure 10.36 Plots of temperature and corresponding bcc and fcc phase fractions with time for (a) 9Cr-3W-3Co-VNb steel with 130 ppm boron, peak temperature of 911°C and (b) Gr.92, peak temperature of 896°C.](image)
on the other hand, the martensitic transformation introduces a high density of dislocations, but recrystallization cannot take place because boron increases recrystallization temperature, Fig. 10.35(e), indicating no production of new GBs. The resultant microstructure of 9Cr-boron steel after PWHT exhibits enough M$_{23}$C$_6$ carbides along PAGBs and block boundaries, which is substantially the same as that of the original microstructure, Fig. 10.35(f), although fine grains form at part of PAGBs of coarse grains. The martensitic transformation takes place also in Gr.92 during cooling. During subsequent PWHT, carbonitrides precipitate preferentially at existing carbonitrides and also at new GBs of fine-grained microstructure, Fig. 10.35(c). The resultant microstructure shows that very few precipitates are formed along PAGBs. The production of new GBs and incomplete dissolution of M$_{23}$C$_6$ carbides are responsible for the very few precipitates along GBs in the fine-grained microstructure after PWHT.

It should be noted that the temperature range for the formation of fine-grained microstructure in Gr.92 is overlapped with that for the very few precipitates along GBs, Fig. 10.38 [42]. This suggests that the observations of fine-grained HAZ provide us an indication of the degradation in creep strength due to Type IV fracture in welded joints, although the reduction of boundary and sub-boundary hardening is more important for the degradation in creep strength than the grain refinement.

### 10.6.3.4 Mechanisms for boron effect

Fig. 10.39 shows the mechanisms responsible for the effect of GB segregation of boron on the suppression of diffusive $\alpha$/$\gamma$ transformation in HAZ of welded joints during heating and on the reduction of coarsening rate of M$_{23}$C$_6$ carbides in the vicinity of PAGBs during creep at 650°C [42]. The segregation of boron at GBs is estimated to be several percent near the $A_{C3}$ temperature of 950°C and to be more than 10% at the creep test temperature of 650°C, as shown in Fig. 10.40. We estimate the equilibrium...
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**Figure 10.38** Schematics of grain size and amount of $M_{23}C_6$ carbides in Gr.92 during simulation heating.

**Figure 10.39** Schematics of (a) GB segregation of boron, (b) diffusive $\alpha/\gamma$ transformation at GB during heating and (c) reduction of coarsening rate of $M_{23}C_6$ carbides by boron during creep.
GB segregation of boron, assuming that initially boron is distributed homogeneously with the concentration $C_i$ as illustrated in Fig. 10.40(a).

After achieving equilibrium GB segregation, the concentration of boron at GBs, $C_{GB}$, is described as

$$C_{GB} = C_0 \exp \left( \frac{B}{RT} \right),$$  \hspace{1cm} (10.13)\)

where $C_0$ is the concentration of boron within grain, $B$ the binding energy between boron and GB, $R$ the gas constant, and $T$ the absolute temperature. Using a binding energy of $B=62.7 \text{kJ/mol}$ [80] reported for type 316 stainless steel, Fig. 10.40(b) shows the concentration of boron at GBs ($C_{GB}$) and inside grains ($C_0$) as a function of temperature, where the initial boron concentration $C_i$ and the grain size are assumed to be 100 ppm and 50 $\mu$m, respectively. At a temperature of 950°C, segregation of several percent of boron can be achieved at GBs.

The GB segregation of boron reduces the interfacial energy $\sigma_{\alpha\alpha}$ for $\alpha/\alpha$ boundary and makes the $\alpha/\alpha$ boundaries less effective as heterogeneous nucleation sites for $\gamma$ phase, Fig. 10.39(b). This retards the diffusive $\alpha/\gamma$ transformation, and hence the martensitic reverse transformation by shear can take place during heating, as already described.

The formation of fine grains at part of PAGBs of coarse grains shown in Fig. 10.34(b) suggests that the nucleation of $\gamma$ phase by diffusive transformation takes place preferentially at part of PAGBs during heating, but the martensitic transformation also takes place at other part of PAGBs during heating [81]. The formation of fine grains by diffusive transformation is limited only at PAGBs of coarse grains because of the retardation effect by boron due to GB segregation. Inside the grain, only martensitic transformation takes place during heating. The nucleation of $\gamma$ phase by diffusive transformation is promoted at GBs because strained regions at GBs enable nuclei to be formed with a much smaller free energy. We think that the driving force for

Figure 10.40 (a) Concentration profile of boron and (b) concentration of boron at grain boundaries ($C_{GB}$) and inside grain ($C_0$) as a function of temperature.
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Diffusive $\alpha/\gamma$ transformation at PAGBs during heating is a little bit larger than or the same as the retardation effect by boron near PAGBs, Fig. 10.41(a). The driving force for diffusive $\alpha/\gamma$ transformation is considered to be much smaller inside the grain than near PAGBs because strained regions are limited near GBs. The retardation effect by boron is also smaller inside the grain than near PAGBs because of no segregation of boron inside the grain. The present results that the martensitic $\alpha/\gamma$ transformation takes place inside the grain during heating suggest that the retardation effect by boron is larger inside the grain than the driving force for nucleation of $\gamma$ by diffusive $\alpha/\gamma$ transformation, Fig. 10.41(a). The concentration of soluble boron in the matrix is estimated to be about 20 ppm by assuming the initial boron concentration is 100 ppm, the enriched boron concentration in $M_{23}C_6$ carbides inside the grain is 0.5%, and the mole fraction of $M_{23}C_6$ carbides is 0.0016 by Thermo-Calc, Fig. 10.41(b). We think that the soluble boron concentration of 20 ppm in the matrix is enough to retard the diffusive $\alpha/\gamma$ transformation, and hence the martensitic $\alpha/\gamma$ transformation takes place inside the grain during heating.

Ostwald ripening of carbides in a solid matrix requires the accommodation of a local volume change around a growing carbide particle because the specific volume of the carbide is larger than that of the alloy matrix [42]. As a small carbide goes into solution, carbon atoms take up interstitial sites in the matrix, and vacancies are created at and near the carbide interface, as shown in Fig. 10.39(c). Then vacancies migrate through the matrix and arrive at a growing carbide interface, which accommodates local volume change. If the enriched boron atoms at PAGBs occupy vacancies around the growing $M_{23}C_6$ carbides, the local volume change cannot be accommodated. This reduces the coarsening rate of $M_{23}C_6$ carbides in the vicinity of PAGB. We think that the main effect due to boron is to occupy vacancies around the growing carbide particles in the vicinity of PAGBs. This makes it difficult to accommodate local volume change.

It is concluded that the enrichment of soluble boron at and near PAGBs by the segregation is essential for the reduction of coarsening rate of $M_{23}C_6$ carbides in the vicinity of PAGBs and for the change in $\alpha/\gamma$ transformation behavior in HAZ from diffusive to martensitic during heating of welding.

Figure 10.41 (a) Schematic drawing of driving force for $\alpha/\gamma$ transformation during heating and (b) boron concentration distribution inside grain.
10.6.3.5 Martensitic 9Cr steel strengthened by boron and MX nitrides: MARBN

Based on the suppression of Type IV fracture using boron and the improvement of long-term creep strength of base metal by using both boron and MX nitride without any formation of BN during normalizing heat treatment, a 9Cr-3W-3Co-0.2V-0.05Nb steel containing 120–150 ppm boron and 60–90 ppm nitrogen was alloy designed. The steel is denoted MARBN, which means martensitic 9Cr steel strengthened by boron and MX nitrides. Fig. 10.42 shows the creep rupture data for the base metal and welded joints of MARBN at 650°C, together with those for P92 and P122 [57]. MARBN exhibits not only much higher creep rupture strength of base metal than P92 and P122 but also substantially no degradation in creep rupture strength of welded joints compared with base metal, indicating no Type IV fracture. MARBN also exhibits enough creep rupture ductility, larger than or same level as T91, because of low nitrogen concentration below 100 ppm; see Fig. 10.24.

Now let us check the alloy design of MARBN for minimization of the degradation in creep strength at long times described in Section 10.4. The GB segregation of boron reduces the preferential microstructure recovery near PAGBs in MARBN. The addition of boron reduces the coarsening rate of $M_{23}C_6$ carbides, which reduces the static recovery of martensitic microstructure. Maruyama and coworkers reported that 9Cr steels are more stable against the static recovery than 12Cr steels [35,36]. With respect to Z phase precipitation, the combination of 9% Cr and low nitrogen concentration of MARBN reduces the driving force for Z phase formation. With respect to impurity effects due to Al and Ni, Al and Ni were minimized in MARBN. While Al was used as a deoxidizing element in the melting process, the concentration of residual Al was intended to be 10 ppm or below. Although excess dislocations after low-temperature

![Figure 10.42 Creep rupture data for MARBN, P92 and P122 at 650°C.](image)
tempering at 700°C or below accelerates the microstructure recovery and degrades the creep strength, the tempering temperature of MARBN was as high as 780–800°C. MARBN contains no δ-ferrite. These stabilize the martensitic microstructure of MARBN during exposure at elevated temperature and minimize the degradation.

Tabuchi and coworkers carried out the creep rupture testing for dissimilar welded joints of MARBN and Ni-base alloys, such as MARBN/Alloy 617 and MARBN/Alloy 263 at 650°C for up to about 30,000 h [82]. The creep rupture strength of MARBN/Alloy 617 and MARBN/Alloy 263 dissimilar welded joints was only a little bit lower than that of MARBN base metal. They observed that a creep crack initiated in the fusion boundary at the lower surface of creep specimen and then propagated toward HAZ. Finally, ductile trans-granular fracture with necking took place in the base metal of MARBN. Their results suggest the fracture mode in dissimilar welded joints is not Type IV fracture.

10.6.3.6 Improvement of oxidation resistance by pretreatment

We have revealed that the addition of 3% Pd significantly improves the oxidation resistance of 9Cr steel in steam at 650°C by the formation of thin scale of Cr₂O₃ [83]. This suggests that the formation of protective Cr₂O₃ scale is possible even for 9Cr steel. However, the application of 9Cr steel containing 3% Pd to main steam pipes of A-USC boilers is economically unfeasible because Pd is very expensive. In NIMS, we have also achieved the formation of protective Cr₂O₃-rich scale on the surface of 9Cr steel by the pre-oxidation treatment in argon (Ar) gas [84,85], by the combination of shot-peening of Cr and pre-oxidation treatment in air at 700°C [86], and by the coating of Ni-(20-50)Cr thin layers [87–91]. In the following, the long-term stability of Cr₂O₃-rich scale formed by the pre-oxidation treatment in Ar gas is described. The oxidation behavior of 9Cr steel in steam at 650°C depends on many factors, such as pre-oxidation temperature and time, oxygen concentration in Ar gas, and minor elements, such as Si.

The sheet specimens having a size of 10 × 20 × 2 mm were cut from bulk materials, which were already heat treated, ground on a SiC paper of 320 grit, rinsed in acetone, and then supplied to the oxidation test in steam. The pre-oxidation treatment was carried out in Ar gas at 500–700°C, using the furnace used for the oxidation test. The Ar gas containing 0.3 ppm oxygen was supplied for the pre-oxidation treatment, except for the experiments examining the effect of oxygen concentration in Ar gas on the subsequent oxidation resistance in steam. The oxidation test was carried out in steam at 650°C for up to a long time exceeding 20,000 h.

The effect of oxygen concentration in the Ar gas supplied for the pre-oxidation treatment on the subsequent oxidation resistance in steam at 650°C was examined using Ar gas containing 0.1 ppm, 0.3 ppm, and 1% oxygen [84,85]. The results are shown in Fig. 10.43. The pre-oxidation treatment was carried out in Ar gas at 700°C for 50 h. The effect of oxygen concentration in the Ar gas becomes more significant with decreasing Si concentration in the 9Cr steel. The weight gain of the 9Cr steel containing 0, 0.3, and 0.5% Si decreases with decreasing oxygen concentration in the Ar gas. The X-ray diffraction experiments for the 9Cr steel after the pre-oxidation treatment show that Cr₂O₃ and Fe₃O₄ form on the specimen surface and that the diffraction
peaks due to Cr$_2$O$_3$ become more dominant with decreasing oxygen concentration in the Ar gas. This suggests that the pre-oxidation treatment in Ar gas containing low oxygen concentration enhances the formation of Cr$_2$O$_3$ scale.

The weight gain in steam at 650°C decreases with increasing pre-oxidation temperature and time. The long-term stability of Cr$_2$O$_3$ scale formed by the pre-oxidation treatment has been examined for the MARB1, MARB2, and MARN steels in steam at 650°C, where MARB1 and MARB2 are 9Cr-3W-3Co-0.2V-0.05Nb steel with 100 and 200 ppm boron, respectively, and MARN is described in Section 6.2. The weight gain curves are shown in Fig. 10.44, where the results after the pre-oxidation treatment in Ar gas at 700°C for 50h are compared with those without pre-oxidation treatment. For the three steels MARB1, MARB2, and MARN, the oxidation resistance in steam is significantly improved by the pre-oxidation treatment, which produces the thin scale of Cr-rich oxides. No evidence was found for the breakaway in the weight gain curves for the specimens with pre-oxidation treatment. The present results indicate that the thin scale of Cr-rich oxides is stable during oxidation in steam at 650°C for a long time exceeding 20,000h. Excellent oxidation resistance of the three steels is also confirmed even in the condition of no pre-oxidation by the Task 3 of DOE Vision 21 project [92].

Fig. 10.45 compares the cross-section of the MARB1, MARB2, and MARN specimens with and without the pre-oxidation treatment, after oxidation test in steam at 650°C for 500h. Without pre-oxidation, the thick scale having a thickness of 50–100 μm forms during oxidation in steam. The major component of the scale is Fe$_3$O$_4$. After the pre-oxidation treatment, the thin scale of Cr$_2$O$_3$ having a thickness of less than 0.1 μm is stable during oxidation in steam. No evidence was found for the exfoliation and cracking of the Cr$_2$O$_3$-rich scale.

The combination of scanning TEM (STEM)-EDS analysis shown in Fig. 10.46(a) and selected area electron diffraction in TEM shown in Fig. 10.46(b) shows that the
Figure 10.44 Weight gain of 9Cr steel MARN, MARB1 and MARB2 with and without pre-oxidation treatment.

Figure 10.45 Cross-section of the steels after oxidation in steam at 650°C for 500h.
major component of the thin scale is $\text{Cr}_2\text{O}_3$ containing a small amount of Fe [84,85]. The Mn-rich layer, identified as $(\text{Fe}, \text{Cr}, \text{Mn})_3\text{O}_4$, is located close to the scale/steam interface. It should be noted that Si ions are enriched along the interface between the Cr-rich oxide scale and alloy matrix. In Fig. 10.46(a), the particles containing high Si and having a size of about 0.1 μm are the precipitates of $\text{Fe}_2\text{W}$ Laves phase but not particles containing Si. The characteristic X-ray images from Si and W cannot be distinguished from each other.

Exfoliation of the thin scale of $\text{Cr}_2\text{O}_3$-rich oxides formed by the pre-oxidation treatment has been investigated by cyclic oxidation test in steam [86]. No

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**Figure 10.46** (a) STEM-EDS analysis and (b) selected area electron diffraction in TEM of cross-section of 9Cr-3W-VNb steel with 0.8% Si after pre-oxidation treatment in Ar gas at 700°C for 50h.
evidence has been observed for the exfoliation of thin scale of Cr$_2$O$_3$-rich oxides up to 40 cycles of cyclic heating and cooling in steam between 150 and 650°C. No difference is observed in weight gain between cyclic and continuous oxidation tests. Further investigation based on cyclic oxidation test under stress will be necessary.

10.6.3.7 Production of MARBN pipe

The production of a large-diameter and thick-section pipe and subsequent fabrication of circumference welds of the pipe have successfully been performed for MARBN [93]. This is based on the collaboration between NIMS and private companies in Japan. A 3-ton ingot, having a size of 785 mm in diameter and 580 mm in height, was prepared by vacuum melting. The ingot was successfully hot-forged to a pipe, which was heat treated and machined to a size of 470 mm in outer diameter, 65 mm in thickness, and 1300 mm in length. The pipe was normalized at 1100°C for 3 h followed by air cooling and then tempered at 780°C for 4 h followed by air cooling. Fig. 10.47(a) and 47(b) show the appearance of the pipe after machining. Circumference welding of the MARBN pipe has successfully been carried out using gas tungsten-arc welding process and using filler wire of Ni-base AWS ER NiCr-3 (Alloy 82). The preheating temperature was kept to be 150°C or more to avoid low-temperature cracking, while the interpass temperature was below 200°C.

![Figure 10.47](image.png)

Figure 10.47 (a) and (b) Appearances of MARBN pipe with 470 mm in outer diameter, 65 mm in thickness and 1300 mm in length, and (c), (d) circumference TIG welding of MARBN pipe.
to avoid high-temperature cracking. After welding, the welded joints were subjected to PWHT at 740°C for 4 h. Fig. 10.47(c) and 47(d) show circumference TIG welding of the MARBN pipe and appearance of welded joints after PWHT, respectively. The creep rupture data for the specimens taken from the pipe were identical to those shown in Fig. 10.42.

10.7 Summary

1. Boundary and sub-boundary hardening gives the most important strengthening mechanism for creep of martensitic 9Cr steel and is enhanced by fine dispersion of precipitates along boundaries. Based on the boundary and sub-boundary hardening, a new martensitic 9Cr steel has been alloy designed for application to thick-section boiler components, such as main steam pipes and headers, with steam temperature of 650°C maximum in coal-fired power plants.

2. The addition of boron and nitrogen to 9Cr-3W-3Co-VNb steel without any formation of BN during normalizing heat treatment improves the long-term creep strength of base metal and suppresses the Type IV cracking in HAZ of welded joints at 650°C.

3. The enrichment of soluble boron at and near PAGBs by the segregation is essential for the reduction of coarsening rate of $M_23C_6$ carbides near PAGBs, which enhances the boundary hardening, and also for the change in $\alpha/\gamma$ transformation behavior from diffusive to martensitic in HAZ of welded joints during heating of welding, which produces approximately the same microstructure between HAZ and base metal. The enhancement of boundary and sub-boundary hardening by fine distributions of $M_23C_6$ carbides along boundaries retards the onset of acceleration creep, which effectively decreases the minimum creep rate and increases the creep life.

4. The addition of excess nitrogen of 300 and 650 ppm to the 9Cr steel with 140 ppm boron causes the formation of a large amount of BN during normalizing, which significantly reduces the soluble boron concentration and accelerates the degradation in both creep strength and rupture ductility.

5. 9Cr-3W-3Co-0.2V-0.05Nb steel with 120–150 ppm boron and 60–90 ppm nitrogen (MARBN) exhibits not only much higher creep rupture strength of base metal than Gr.91, Gr.92, and Gr.122 but also substantially no degradation in creep strength due to Type IV fracture in HAZ of welded joints at 650°C.

6. The formation of protective $Cr_2O_3$-rich scale is achieved on the surface of MARBN by pre-oxidation treatment in argon gas. This significantly improves the oxidation resistance of MARBN in steam at 650°C.

7. MARBN is suitable as thick-section boiler components for long-term service at steam temperature of 650°C in coal-fired power plants.

References


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