Alloy development for high Cr martensitic steel
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PhD Thesis
Alloy development for high Cr martensitic steel

by

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To the warm memory of my grandad, E.G. Fedulov.
Preface

The present PhD thesis is submitted in partial fulfillment of the requirements for a PhD degree at the Department of Mechanical Engineering, Technical University of Denmark (DTU). The work presented in this thesis was carried out during the period November 2015 to November 2018. The work was conducted under the supervision of Professor John Hald from the Department of Mechanical Engineering, DTU. The PhD project was part of the following projects: KME, CRESTA. The project was financially supported by Siemens AG.
Abstract

Steam power plants burning fossil fuels (coal, oil, natural gas) generate most of the global electricity, and in countries such as China, India, Russia and Poland fossil fired power plants generate 80% or more. Though huge efforts are made to transform power production to renewable energy such as wind and solar, fossil power will still have roles in coming decades to maintain weather-independent power supply and to provide cheap and reliable electrification in developing countries.

The efficiency and harmful emission from steam power plants are highly dependent on the operating parameters, such as steam temperature and pressure, which are limited by the properties of engineering materials used in high temperature components such as turbines, pipes and castings. Creep resistant martensitic 9-12% Cr steels are preferred materials because of their excellent combination of high creep strength, corrosion resistance and relatively low cost. The strongest commercial steels available today are 9% Cr steels, which allow steam temperatures up to 620 °C. Efforts are ongoing to increase steam temperatures to 650 °C by improving the creep strength and corrosion resistance of the martensitic steels. Corrosion resistance is achieved by increasing of the Cr content up to 11-12%. However, so far the alloy concepts for creep resistant 11-12% Cr steels have failed, since they relied on precipitation strengthening from fine MX ((V,Nb)(C,N)) carbonitrides, which transform into coarse Z-phase (Cr(V,Nb)N) nitrides causing a loss of precipitation strengthening and creep strength breakdown.

In the present PhD project a promising alloying concept combining reduced nitrogen and added boron to provide microstructure stability of 9-12% Cr martensitic steels is investigated. The aim of the research is to improve the understanding of strengthening mechanisms in low
nitrogen martensitic steels. Investigations were made in two directions: microstructure characterization of new experimental 11% Cr martensitic steels and study of boron behavior in various 9-10% Cr martensitic steels.

Four 10-11.2% Cr tempered martensite steels alloyed with nitrogen, titanium and boron were investigated after long-term aging and creep. Their microstructure evolution was characterized by transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS). It was found that slight differences in the contents of nitrogen and titanium significantly affect the microstructure stability and creep behavior. When all nitrogen in the steels is tied up as TiN the creep strength is low. If free nitrogen is available after TiN formation high creep strength and microstructure stability can be achieved for 10% Cr steels, presumably by the formation of fine nitrides. In 11.2% Cr steels with free nitrogen available after TiN formation, Z-phase formation led to creep strength breakdown after 3,000-5,000 h at 650 °C.

The studies of boron comprised development of a site-specific sample preparation technique using focus ion beam milling, which allowed speeding up of successful sample fabrication for atom probe tomography (APT). Detailed investigations of boron segregation behavior during normalizing from 1100 °C were made on three martensitic steels containing 10 ppm, 70 ppm and 100 ppm of boron. Fine $M_2B$ borides (15×70 nm) were found to form on prior austenite grain boundaries during normalizing of the 100 ppm boron steel. Lower boron content did not show such boride formation. APT measurements showed that boron segregated to austenite grain boundaries in similar concentrations (0.8 at.%) in the 10 ppm boron and the 70 ppm boron steels, but significant amounts (25-40%) of the added boron remained in the grain center after normalization. Half (45-55%) of the added boron in the 10 ppm boron and 70 ppm boron steels was located by the APT measurements. In the 10 ppm boron steel the remaining boron was found to form boronitrides.

The measured concentration profiles near boundaries did not fit to profiles predicted from theoretical models of diffusion limited equilibrium segregation or non-equilibrium segregation. The present quantitative study of boron segregation provides data, which are believed to be highly useful for the optimization of boron additions to the creep resistant martensitic steels. It should be followed up with further quantitative studies of boron behavior during tempering and creep.
Résumé

Fossilt fyrede dampkraftværker som afbrænder kul, naturgas eller olie genererer størstedelen af verdens elektricitet, og i lande som Kina, Indien, Rusland og Polen står fossile kraftværker for over 80% af produktionen. Selvom man gør enorme indsatser for at omstille elproduktionen til fornybar energi som vind og sol, vil den fossile produktion stadig spille vigtige roller i de kommende årter, dels ved at levere grundlast uafhængig af vejret og dels ved at levere en billig og pålidelig kilde til elektrificering af udviklingslande. Effektiviteten af og skadelige emissioner fra dampkraftværker bestemmes i høj grad af driftsparameetre som dampstemperatur og -tryk, der begrænses af egenskaberne for de materialer, der anvendes i højtemperaturkomponenter som turbiner, dampledninger og støbninger. Krybestandige martensitiske 9-12% Cr stål er foretrukne materialer til disse komponenter på grund af høj krybestyrke god korrosionsbestandighed og lav pris. De stærkeste kommercielt tilgængelige stål i dag er 9% Cr stål, som tillader dampstemperaturer op til 620 °C. Man bestræber sig på at hæve dampstemperaturen til 650 °C ved at forbedre krybestyrke og korrosionsbestandighed for de martensitiske stål. Korrosionsbestandigheden forøges ved at hæve kromindholdet til 11-12%. Imidlertid er alle de hidtil udtænkte legeringer med 11-12% Cr mislykkedes, idet de beror på udfældningshærdning fra fine (V,Nb)(C,N) karbonitrides, der omdannes til grove Z-fase (Cr(V,Nb)N) nitrides, som bevirker tab af udfældningshærdning og nedbrud af krybestyrken. I det foreliggende ph.d. projekt undersøges et lovende legeringskoncept, der kombinerer et meget lavt indhold af kvælstof med bor i 9-12% Cr stål for at tilvejebringe mikrostruktur stabilitet. Studierne sigter mod at forøge forståelsen af styrkegøende mekanismer i krybestandige stål med lave indhold af kvælstof. Undersøgelserne om-
fatter dels mikrostruktur karakterisering af nye eksperimentelle martensitiske 11% Cr stål og dels studier af bors opførsel i forskellige martensitiske 9-10% Cr stål. Fire 10-11.2% Cr martensitiske stål legeret med kvælstof, titaniu m og bor blev undersøgt efter langtids ældning og efter krybning. Deres mikrostruktural udvikling blev undersøgt med transmissions elektromikroskopi (TEM) og energidispersiv røntgenspektroskopi (EDS). Det blev fundet, at ganske små forskelle i indhold af kvælstof og titaniu m havde stor indflydelse på mikrostruktur stabilitet og krybestyrke. Når alt tilgængeligt kvælstof i stålene er bundet som TiN er krybestyrken lav. Når der er frit tilgængeligt kvælstof efter TiN dannelse kan man opnå høj krybestyrke i 10% Cr stål, formentlig ved udfældning af fine nitrider. I stål med 11.2% Cr og med frit tilgængeligt kvælstof efter TiN dannelse medfører Z-fase dannelse nedbrud af krybestyrken efter 3.000-5.000 timer ved 650°C.

Studierne af bor omfattede udvikling af en teknik til prøveudtagning lokalt i mikrostrukturen ved anvendelse af ionstråler (FIB), som tillod hurtigere prøvetilberedning til atom probe tomografi (APT). Detaljerede undersøgelser af bor sejring under normalisering fra 1100°C blev udført på stål med 10 ppm, 70 ppm og 100 ppm bor. Det blev fundet, at fine M₂B borider (15 x 70 nm) dannes på austenit korngrænser under normaliseringen af 100 ppm bor stålet. Stålene med lavere borindhold udviste ikke sådanne borider.

APT målinger viste, at bor sejrer til austenitkorngrænser i samme koncentration (0.8 atom%) i stålene med 10 ppm og 70 ppm bor, men en væsentlig andel af det tilsatte bor forbliver i midten af kornene efter normalisering. Halvdelen (45-55%) af det tilsatte bor til 10 ppm og 70 ppm bor stålene blev lokalisert med APT målingerne. I 10 ppm bor stålet blev det tiloversblevne bor fundet som bornitrider.

De måltte koncentrationsprofiler nær korngrænser stemte ikke overnes med profiler forudsagt på basis af teoretiske modeller af diffusions begrenset ligevægtssejring eller ikke-ligevægts sejring. Det foreliggende kvantitative studium af borsejring tilvejebringer data, som forventes at være meget anvendelige til at optimere tilsætningen af bor til krybebe standige martensitiske stål. Det bør følges op af videre undersøgelser af bors opførsel under varmebehandling og krybning.
First and foremost, I would like to thank my supervisor, Prof. John Hald, for valuable advices, inspiring discussions and source of knowledge and motivation given to me throughout the past 3 years. John, it was a privilege to conduct my PhD work under your supervision, being continuously guided from the first day of this exciting and challenging project and being introduced to the intelligent and inspiring people from the relevant field. I am especially thankful not only for your indisputable professionalism in the field of high-temperature materials, but also for being enthusiastic, kind and open person, who is pleasant to work with.

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Chapter 1

Introduction

1.1 Energy security

Energy is one of the most important necessities of life nowadays. The driving force for increasing global electricity production is the growth of human population in the world. However, power production has to face with energy security combined with environmental protection issues, especially since the emission of harmful gases such as carbon dioxide $\text{CO}_2$ has been linked to global warming. In order to protect human health and the environment for future generations there is a trend to substitute fossil fuels for the renewable energy resources, such as wind and solar power, which do not emit $\text{CO}_2$ to the atmosphere. Green energy stations have increased dramatically in some European countries, e.g. in Denmark wind contributes about 40% of electricity production. Though people make a lot of efforts supporting clean and renewable electricity production, sufficient electricity supply for the entire society involving only green energy at the current moment and for the next 10 years is not likely to be achieved. Power plants working by burning fossil fuels (coal, oil, natural gas) will still be operating as a weather-independent power supply. Moreover, coal-fired power plants are not yet substitutable in the regions where high amount of electricity is required, and it is expected to be so for the next decades since coal is the cheapest source for electricity production in the population increasing parts of the world [1, 2, 3, 4]. Cost-minimizing of electric power generation as well as limitation of fuel consumption and environmental pollution should
be reached through the improvement in the thermal efficiency of power plants.

Fig. 1.1 represents a schematic drawing of a steam power plant. The fuel (coal) is burned producing hot steam in a boiler, then the high temperature and pressure steam moves by steam line to the turbine, where it rotates blades of a turbine, thus, generating electricity via a generator.

In principle, thermal power plants work according to the Carnot cycle, whereby the thermal efficiency, \( \eta \), of a heat engine is defined as work done by this engine, \( W \), divided by heat input, \( Q_h \). After applying thermodynamic laws, the formula for the thermal efficiency may be rewritten as:

\[
\eta_{\text{Carnot}} = 1 - \frac{T_c}{T_h},
\]  

(1.1)

where \( \eta \) is efficiency of Carnot cycle, \( T_c \) is absolute temperature of a cold reservoir and \( T_h \) is absolute temperature of a hot reservoir.

The higher difference between \( T_h \) and \( T_c \), the more energy can be extracted. However, the Carnot efficiency is idealized and cannot be reached in the real power plants. Instead, the Rankine cycle, which converts heat into mechanical work, must be used in practice. In this
case, $T_h$ and $T_c$ are steam entry and steam condenser temperatures, respectively. Normally, Rankine cycles consist of four processes. In the beginning water is pumped from low to high pressure; then it is heated in a boiler by heat source (coal) forming supersaturated steam; after that supersaturated steam enters in a turbine generating power; and finally it is condensed on a condenser forming liquid again. Higher efficiency is achieved by higher steam temperatures and pressures.

Efficiency increases have been achieved since the 1980s by introducing supercritical and ultra-supercritical (USC) power plants with significantly enhanced steam parameters (steam temperature and pressure). Supercritical power plants at pressures higher than 22 MPa and power plants working at steam temperatures higher than 540 $^\circ$C and steam pressures more than 24.1 MPa are called USC power plants. Modern power plants established in Japan, China, Europe and USA enable operation up to 610 $^\circ$C and 285 bar for live steam and up to 620 $^\circ$C for reheating steam. Transition from the traditional steam parameters of 538 $^\circ$C and 167 bar to the advanced USC ones of 620 $^\circ$C and 285 bar gave a leap in power plant efficiency from 38% to 45%. Further improvement in efficiency and performance of fossil fuel power plants requires the development of new materials able to withstand extremely high operating conditions, and having certain properties such as:

- creep rupture strength ($10^5$ h creep rupture strength at 100 MPa at the required operating temperature);
- high oxidation resistance;
- low thermal expansion;
- high yield strength;
- high heat conductivity;
- good creep rupture ductility;
- weldability;
- low cost.

The 9-12 % CrMoV martensitic steels, used for power plant applications since 1950s, have been identified as advantageous materials with
a room for improvements. For comparison, austenitic steels have lower thermal conductivity and thermal expansion coefficient. Ni-base superalloys have been found to enable operating temperature of 700 °C and above, however Ni-base superalloys are much more expensive in comparison with martensitic steels. Thus, 9-12% Cr martensitic steels have been recognized as a key materials for the critical components of power plants, such as boilers and turbines [6, 7, 8, 9].

There is a constant need for increasing the efficiency of power plants to provide more and cheaper electricity, at the same time decreasing the pollution in the atmosphere conditioned by an emission of CO₂. The present work addresses new ideas for the further development of new 9-12% Cr martensitic steels, which is crucial to the power industry.

1.2 Scope of the PhD Thesis

This Ph.D thesis is structured in 7 individual chapters. Figure 1.2 shows a flowchart of the dissertation, which is written in the manuscript-collection way.

Chapter 1 called ”Introduction” states the overall basis for conducting the present Ph.D work including reasons and motivation for research.

Chapter 2 ”Background” gives a literature review on the studied subject.

Chapter 3 states motivation and objectives of present PhD project. Results obtained during this research are given in chapter 5 and presented as 5 individual manuscripts.

Further the doctoral thesis is continued with discussion of experimental research (”Chapter 6”), main conclusion (”Chapter 7”) and a proposal for further work (”Chapter 8”). Finally, two appendices complete this work.
Figure 1.2: Flowchart of the dissertation work.
Bibliography


Chapter 2

Background

2.1 History and applications of 9-12% Cr steels

Historically, the development and production of 9-12% Cr martensitic steels began in 1912 when 12% Cr steel modified by 2-5% of Mo was produced in Germany. Before that, non-alloyed steels were used in steam zones of power plants operating at max. 350°C and 15 bar. In 1920s low-alloyed steels able to serve at 450°C and 35 bar were introduced. After that many research activities were going on in an attempt to improve creep strength and corrosion resistance by optimizing Mo, Mn, Si and V alloying elements [1, 2, 3].

In general, there are 5 “generations” of 9-12% Cr steels so far beginning with the T9 steel (9Cr1Mo) developed in 1940s. This steel has shown creep rupture strength of 40 MPa at 600 °C for 10^5 h and is assigned as “generation 0” steel. The 9-12% Cr martensitic steels, gradually developed from generation 0 to 5, along with their chemical compositions are presented in Table 2.1 [4].

Generation 1 steels were introduced in 1960s and based on 12CrMoV alloying concept. Improved creep strength of the steel X20 was achieved by precipitate strengthening from M \textsubscript{23}C \textsubscript{6} carbides. The creep rupture strength of the 1st generation steels increased to 60 MPa at 600 °C for 10^5 h, which enable the construction of the first supercritical steam power plants in the 1980s with steam parameters of 25 MPa and 540 °C. [1, 5].

Generation 2 is characterized by T/P91 steel widely used nowadays
in pressure vessel and piping systems. This steel was developed in 1970s in USA as a result of optimization of C, Nb, V, N alloying elements. Steels of this generation exhibit creep strength up to 90 MPa at 600 °C for $10^5$ h. This enabled construction of the first USC power plants operating at steam temperatures up to 600 °C[5, 6].

The further modification of T91 led to the development of generation 3 steels in 1980s-1990s. This generation is represented by Japanese T/P92 steel, European T/P911 steel, and Japanese P122 steel. The creep rupture strength of these steels increased to 115 MPa at 600 °C for $10^5$ h, which allowed power plant operation up to 620 °C and 300 bar. These steels are alloyed with C, Si, Mo, W, V, Nb, N. In addition, B is added in some of the generation 3 steels. The P92 steel is currently the strongest commercial steam pipe steel.

In 1990s further studies were focused on designing generation 4 steels allowing the operation at higher than 620 °C. For that reason, Cr content was enhanced to 11-11.5 w.% to improve corrosion resistance. Also W and Co were found to be effective for precipitate stability and their contents were subsequently increased. Generation 4 is presented by NF12 and SAVE12 steels developed in Japan. However, the steels showed dramatic degradation in creep strength compared to the previous grade steels. Their creep rupture strength at 600 °C for $10^5$ h was only 90-95 MPa. The reason for the drop in creep strength was explained by transformation of fine V and Nb MX nitrides to coarse Cr(V,Nb)N Z phase, causing to severe loss of precipitation strengthening. It was found that increased Cr content accelerated the formation of Z-phase [35].

Generation 5 of the 9-12% Cr martensitic steels has been under development since the beginning of the 2000s. Generation 5 steels are intended for application at 650 °C and expected to have creep rupture strength of 120-140 MPa at 600 °C for $10^5$ h [7]. There are two main approaches to reach the stated goal: to avoid Z phase precipitation forming in steels during their long-term high-temperature exposure or to use fine distributed Z phase and further suppress its coarsening. Research projects on Z-phase strengthening steels are currently going on in Denmark and Sweden. The idea of such alloy design is distributing of fine Z-phase precipitates already after tempering, which should provide long precipitate strengthening. For that reason, Cr is increased to 12%, C is lowered as much as possible [8, 9].
Table 2.1: Chemical composition of some martensitic steels and their creep rupture strength at 600 °C [4].

<table>
<thead>
<tr>
<th>Country Generation</th>
<th>Steel</th>
<th>Chemical composition (w.%)</th>
<th>Rupture strength at 600 °C (MPa)</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>Cr</td>
</tr>
<tr>
<td>Basic steels</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Germany 1</td>
<td>X22CrMoV 12</td>
<td>0.22</td>
<td>12.0</td>
</tr>
<tr>
<td>UK</td>
<td>H46</td>
<td>0.16</td>
<td>11.5</td>
</tr>
<tr>
<td></td>
<td>FV448</td>
<td>0.13</td>
<td>10.5</td>
</tr>
<tr>
<td>France 3</td>
<td>56T5</td>
<td>0.19</td>
<td>11.0</td>
</tr>
<tr>
<td>Japan 4</td>
<td>TAF</td>
<td>0.18</td>
<td>10.5</td>
</tr>
<tr>
<td>USA 5</td>
<td>11%CrMoVNBn</td>
<td>0.18</td>
<td>10.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Advanced steels</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>USA 6</td>
<td>P91</td>
<td>0.10</td>
<td>9.0</td>
</tr>
<tr>
<td>Japan 7</td>
<td>HCM 12</td>
<td>0.10</td>
<td>12.0</td>
</tr>
<tr>
<td>Japan 8</td>
<td>TMK 1</td>
<td>0.14</td>
<td>10.3</td>
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<td></td>
<td>TMK 2</td>
<td>0.14</td>
<td>10.5</td>
</tr>
<tr>
<td>Europe 9</td>
<td>X18CrMoVNBn</td>
<td>0.18</td>
<td>9.5</td>
</tr>
<tr>
<td></td>
<td>91</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Europe 10</td>
<td>X12CrMoWVNBn</td>
<td>0.10</td>
<td>10.3</td>
</tr>
<tr>
<td></td>
<td>E911</td>
<td>0.11</td>
<td>9.0</td>
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<tr>
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<td>P92</td>
<td>0.07</td>
<td>9.0</td>
</tr>
<tr>
<td>Japan 12</td>
<td>P122</td>
<td>0.10</td>
<td>11.0</td>
</tr>
</tbody>
</table>

1.0 Cu
The Z-phase strengthening approach is out of the scope of the present PhD project, which focuses on methods for improving the creep strength by avoiding Z-phase precipitation. Since Z-phase is a nitride, the general principle of avoiding the formation of Z-phase in 9-12% Cr martensitic steels involves an extreme decrease of the N content. This approach was first used in Japan by NIMS (National Institute of Materials Science) in 2000s, which led to several new experimental steels. Since that, the concept of lowering nitrogen was adopted for further investigations in Japan, Europe and Russia. Though this approach worked sufficiently well in steels with 9% of Cr, it is unlikely that these steels will have enough oxidation resistance for application at higher temperatures [8, 10, 11, 12]. In addition to the low-nitrogen approach, it is worth to notice on complementary to the avoiding of Z-phase, the addition of boron for the further creep strength improvement has shown high potential. Since the optimized concentration of B and N can give great improvements in creep strength, this alloying design concept is considered as very promising and is explored in the martensitic steels studied in the present PhD project.
2.2 Metallurgy of 9-12% Cr martensitic steels

2.2.1 Heat treatment

Heat treatment (HT) controls the microstructure of materials and, therefore, affects their mechanical properties. A proper selection of HT parameters is essential in obtaining the desired properties. The HT of 9-12% Cr martensitic steels usually consists of quenching (or normalization) and tempering. During normalization, steel is heated up above $Ac_3$ into the austenitic region where the steel acquires face-centered cubic (FCC) structure (Fig. 2.1), hold there and then cooled down to the room temperature. The holding temperature and time should be selected sufficiently for homogenization of all alloying elements and at the same time dissolving agglomerations and coarse phases formed during solidification. Moreover, it should not be extremely high in order to prevent the excessive grain growth and formation of $\delta$-ferrite.

The Fe-Cr system diagram, presented in figure 2.1a, shows that Cr restricts the $\gamma$ loop. In the Cr range of 12-13%, the $\alpha + \gamma$ phase is present and after 13% of Cr ferrite phase occurs at all temperatures. However, the addition of C up to 0.2 w.% into Fe-Cr system expands the $\gamma$ region to higher Cr contents (up to 15 w.%) as well as widens the $\alpha + \gamma$ range up to Cr content of 18 w.%. Fig. 2.1b shows the Fe-Cr-C diagram for 0.1 w.% of carbon.

In creep-resistant martensitic steels many additional alloying elements are present, which can affect the transformation temperatures
Background

(specifically $A_3$ and $A_4$) in the phase diagram. In this respect alloying elements are classified based on their effect on the austenite stability as ferrite ($\alpha$) and austenite ($\gamma$) forming elements [2].

Ferrite stabilizing elements: Cr, Mo, W, Si, V, Nb, Ti.

Austenite stabilizing elements: Mn, Ni, Cu, Co, C, N, B.

There is a high importance in keeping the right balance between austenite and ferrite stabilizing elements, otherwise $\delta$-ferrite may be present in the martensitic microstructure which may lead to embrittlement. To avoid that, Ryu and Yu [17] provided an equation predicting the quantity of $\delta$-ferrite in martensitic steels:

$$Cr_{reg} (%) = Cr + 0.8Si + 2Mo + 1W + 4V + 2Nb + 1.7Al + 60B +$$
$$+ 2Ti + 1Ta - 2Ni - 0.4Mn - 0.6Co - 0.6Cu - 20N - 20C, \quad (2.1)$$

where $Cr_{reg}$ should be $< 12\%$ in 9\%Cr steels and $< 4\%$ in 12\%Cr steels.

Depending on the cooling parameters (cooling rate and chemical composition of material) either diffusion (ferrite, pearlite or bainite) or diffusionless (martensite) transformation takes place. Figure 2.2 shows the Continuous cooling transformation (CCT) diagram for 9\% Cr martensitic steel P92. In 9-12\% Cr steels complete martensite transformation takes place at relatively slow cooling rates (air cooling).

The martensitic transformation from austenite begins at the martensite start temperature ($M_s$). Thereafter, the volume fraction of martensite increases with decreasing temperature until the martensite finish temperature ($M_f$) is reached, corresponding to the martensite fraction of 100\%.

The following equation is normally used in order to calculate the temperature $M_s$ in 9-12\% Cr martensitic steels:

$$M_s(\circ C) = 550\circ C - 450C - 33Mn - 20Cr - 17Ni - 10W - 20V -$$
$$\quad - 10Cu - 11Nb - 11Si + 15Co, \quad (2.2)$$

where the concentration of each element should be inserted in w.\%.

Usually the temperature $M_s$ lays between 200-450 $\circ C$ in different alloys. However, almost all alloying elements (except for Co) reduces the temperature $M_s$ in 9-12\% Cr martensitic steels.
Depending on the alloy composition, martensite can form in the shape of laths or plates. The carbon concentration in steel plays a major role in the formation of the martensite morphology. It has been experimentally observed that martensite in the lath shape appears in low carbon steels while in the plate shape - in high carbon steels [23].

Since carbon atoms have a limited time for back diffusion during martensite transformation, they may remain supersaturated within the lattice. These interstitial carbon atoms extend martensitic lattice along one direction thus forming a body-centered tetragonal cell. The martensite obtained after normalization is normally hard and brittle, the hardness value of as-normalized 9-12% martensitic steels is approximately 400 HV and increases with increase in carbon content.

Such hard and brittle martensite phase has to be softened by tempering [HT]. During tempering, 9-12% Cr steels are usually heated up below Ac1 (720-800 °C), hold for a certain time cooled down to the room temperature. Typical hold times are in the order of 2-5 h for steam pipe (<100 mm section thickness), whereas large components like turbine rotors require much longer tempering up to several days. The tempering temperature is normally selected with respect to the properties required for the certain application. Low tempering temperatures are used for turbine rotors in order to obtain high tensile strength, and high tempering temperatures are used for steam pipes, where high toughness is necessary [14, 24]. Since some elements, such as Ni and Mn, can signif-
Figure 2.3: Schematic illustration of tempered martensitic microstructure of 9–12% Cr steels [25].

Figure 2.4: TEM foils illustrate a typical martensite microstructure evolved in 9-12% Cr martensitic steels after: normalization (a) and tempering (b) HT (on example of 10% Cr martensitic steel).

icantly lower the $A_1$ temperature, the formation of reversed austenite can occur during tempering, which is detrimental for toughness.

A typical hardness value of 9-12% Cr steels after tempering is approximately 220-250 HV. The microstructure obtained by HT containing normalization and tempering, is called tempered martensite. It consists of martensite packets, blocks and laths, decorated by secondary phase precipitates (usually carbides and carbonitrides) (Figs. 2.3, 2.4).
2.2 Metallurgy of 9-12% Cr martensitic steels

2.2.2 Precipitates in 9-12%Cr martensitic steels

Precipitation process in 9-12% Cr martensitic steels is essential since it is responsible for the microstructure stability and, therefore, mechanical properties of steel components. Some precipitates of secondary phase form during tempering and some of them – during high-temperature exposure and creep. However, they all go through the 3-stage path: nucleation, growth and coarsening.

Nucleation

Nucleation is important in the precipitation process because it affects the precipitation distribution and, therefore, microstructure stability of steels. If the nucleation rate is relatively high, many fine precipitates form, if precipitates have slow nucleation rate, few coarse precipitates form resulting in the poor creep properties. The nucleation rate usually depends on the thermodynamic driving force and the interfacial energy of the nuclei. Critical size of nuclei (size, after which its dissolution is energetically not beneficial and immediate growth is inevitable) can be estimated by:

\[
r^* = \frac{2\gamma V_m}{-\Delta G_m},
\]

where \( \gamma \) is interfacial energy, \( V_m \) is molar volume of the precipitate phase and \( \Delta G_m \) is driving force for precipitation.

Nucleation of precipitates can occur by homogeneous or heterogeneous mechanisms. The heterogeneous nucleation is often quicker since from the thermodynamic point of view it is beneficial to nucleate on crystallographic defects, such us dislocations, GBs or other precipitates causing a reduction of the interfacial energy. The homogeneous nucleation occurs away from a surface and may be triggered by the fluctuation of material composition on the atomic level.

Growth

After the nuclei have reached their critical size, precipitates grow increasing their volume fraction. The growth rate of precipitates is generally controlled by their driving force and diffusion of critical elements.
Coarsening

During the last stage of precipitation, named coarsening (or Ostwald ripening), coarse precipitates grow by consuming fine ones. The volume fraction (total amount) of precipitates remains at the same level but the size distribution changes with time. The driving force for this process is the difference in the solubility and concentration of alloying elements depending on the surface curvature, which leads to a concentration gradient between fine and coarse precipitates [43]. Generally, each thermodynamic system tends to reduce the total interfacial energy and, therefore, the presence of a few coarse particles (since they have a less total surface in comparison with the total surface from many small precipitates) is more energetically beneficial.

The coarsening rate is described as:

$$D^n_t - D^n_0 = kt,$$  \hspace{1cm} (2.4)

where $D_t$ is the size of the particle at the time $t$, $D_0$ is the initial size of the particle, $k$ is the rate constant, which depends on the interfacial matrix/particle energy, the equilibrium concentration of the necessary elements in the matrix, the volume fraction of precipitates and other factors, $n$ is time exponent [44, 45].

Coarsening rate of precipitates, in its turn, depends on the rate controlling mechanism: for volume diffusion controlling mechanism $n = 3$; for grain boundary diffusion controlling mechanism $n = 4$. In the first case, the coarsening rate can be determined as [14]:

$$k = \frac{8}{9} \times \frac{\gamma V_m}{\sum_{i=1}^c [(\chi_i^\beta - \chi_i^{\alpha/\beta})^2 / (\chi_i^{\alpha/\beta} D_i / RT)]},$$ \hspace{1cm} (2.5)

where $\gamma$ is interfacial energy, $V_m^\beta$ is molar volume of the precipitate phase, $D_i$ is diffusion coefficient of element $i$ in the matrix, $\chi_i^\beta$ is molar fraction of element $i$ in the precipitate and $\chi_i^{\alpha/\beta}$ is the molar fraction of element $i$ at the precipitate/matrix interface.

When particle coarsening occurs by GB diffusion controlling mechanism, the coarsening rate will depend additionally on GB diffusivity, width of GB, and segregation factor.

Since the fine precipitate distribution is essential for good strength and long-term creep properties, the coarsening process results in degra-
differentiation of the martensite microstructure and the breakdown of materials. Different kinds of precipitates in 9-12% Cr martensitic steels have different growth and coarsening rates. Fig. 2.5 shows a typical distribution of secondary phase precipitates during high-temperature exposure for 16000 h in 9% Cr martensitic steel that represents an evolution of precipitates with clearly seen stages of nucleation, growth and coarsening.

Metastable precipitate phases

Depending on the chemical compositions and the tempering temperatures various metastable precipitates may nucleate in 9-12% Cr martensitic steels during tempering. Some of them, such as $M_2C$, $M_2C$, $M_7C_3$, may have a very short lifetime and can be replaced during the tempering process by the thermodynamically stable carbide $M_{23}C_6$. Meanwhile, other precipitates, such as MX carbonitrides, can exist for decades during creep and are then replaced by Z-phase in high Cr martensitic steels during service. In the 9% Cr martensitic steels containing Ni in the
amount of 0.7-1.5 w.%, the following sequence was observed:

$$\text{M}_3\text{C} \rightarrow \text{M}_2\text{C} \rightarrow \text{M}_{23}\text{C}_6$$

and in the martensitic steels containing Ni in the amount of < 0.7 w.% a different sequence is found:

$$\text{M}_3\text{C} \rightarrow \text{M}_7\text{C}_3 \rightarrow \text{M}_{23}\text{C}_6 \ [26, 27].$$

In some 9% Cr martensitic steels metastable cementite of $\text{M}_3\text{C}$ is often transformed directly into $\text{M}_{23}\text{C}_6$ during tempering, while in others - $\text{M}_{23}\text{C}_6$ carbides nucleate on the grain boundaries in the shape of thin films and then transform into spherical particles $[28]$.

### 2.2.3 Stable precipitate phases

#### $\text{M}_{23}\text{C}_6$ carbides

$\text{M}_{23}\text{C}_6$ is a stable Cr-rich carbide with FCC structure which precipitates on the martensite lath, packet and Prior austenite grain boundary (PAGB)s and dissolves previously formed metastable carbides. Precipitates of $\text{M}_{23}\text{C}_6$ may also have minor content of W, Mo, V, Fe, and B $[29]$. The average size of these carbides after tempering of 9-12% Cr martensitic steels is about 70 – 150 nm, after annealing and creep exposure $\text{M}_{23}\text{C}_6$ carbides tend to coarsen significantly $[8, 30, 31]$. On the other hand, fine distribution of $\text{M}_{23}(\text{C,B})_6$ carbides during long-term creep was achieved by the addition of boron, and thus, in boron-added martensitic steels, the creep strength was found to be increased. However, the mechanism of the effect of B on the lowering of the coarsening rate of $\text{M}_{23}(\text{C,B})_6$ carbides during creep is still unknown.

#### MX carbonitrides

MX-type carbonitrides (where M is Ti, Nb, V, Ta, and X is C, N) precipitate homogeneously distributed within the martensite matrix and have fcc structure. In 9-12% Cr martensitic steels MX carbonitrides precipitate during tempering in form of small particles with average size of 30-70 nm (secondary precipitates) or remain undissolved after solidification or normalisation (primary coarse carbides, often NbC and TiC) $[28, 32]$. MX carbonitrides have relatively slow coarsening rate and enhance creep strength by pinning free dislocations and sub-grain boundaries during creep $[33]$. The optimal relationship between Nb and
V in 9-12% Cr martensitic steels is of high importance since it provides thermodynamically stable two-phase separation of carbonitrides. This separation of carbonitrides enhances their stability against coarsening at elevated temperatures. The coarsening and gradual transformation of nanosized MX precipitates into the large and harmful Z-phase with the size of several hundred nm results in creep strength degradation of 9-12% Cr steels during high-temperature exploitation [9, 31].

Z-phase

Cr(V,Nb,Ta)N precipitates of Z-phase are stable nitrides which form at the expense of MX nitrides during long-term exposure at elevated temperatures. Z-phase is found to have tetragonal structure [34], however, cubic structure or coexistence of cubic and tetragonal structures were found after relatively short time exposure, as reported in [35, 36]. Z-phase precipitates as coarse particles which do not contribute to precipitation hardening, and since it consumes fine and beneficial MX nitrides after long exposure time, a significant drop in creep strength is inevitable. The replacement of MX precipitates by Z-phase is a slow process in 9% Cr martensitic steels compared to 12% Cr martensitic steels and may take decades, thus, Cr content is a crucial factor in the precipitation rate of Z-phase. Recently, several attempts to develop 12% Cr martensitic steels based on the use of Z-phase as strengthening agent were made. It was obtained by fast transformation of MX precipitates into Z-phase during tempering. In order to gain fast transformation, V should be replaced by Nb or Ta. The best results were reported with Ta-containing CrTaN Z-phase, however, the coarsening rate was found to be much higher in comparison with MX precipitates [9].

Laves phase

(Fe,Cr)₂(Mo,W) precipitates of Laves phase form during exposure at elevated temperatures in the 9-12% martensitic steels containing Mo and W. They may also precipitate during tempering when the contents of W and Mo are relatively high. Laves phase is an intermetallic phase with a hexagonal crystal structure, which often precipitates as relatively coarse particles on the martensite lath, packet and block boundaries as well as PAGB, without any strict orientation relationship with martensite
Figure 2.6: TEM carbon replica illustrates the most frequently observed precipitates in 9-12% Cr martensitic steels on the example of experimental 0.02C-9Cr alloy subjected to creep test at 650 °C for 1500h (a) and 16000 h (b) [42].

[37]. W-containing Laves phase is found to nucleate faster and more finely distributed as compared to the Mo-containing Laves phase [38, 39, 40]. The presence of Si and Cu accelerates the nucleation of Laves phase in 9-12% Cr martensitic steels [41]. The precipitation of Laves-phase occurs by expense of Mo and W, which are removed from the matrix, that results in loss of solid solution strengthening. However, a fine distribution of Laves-phase particles (during short-term creep) can provide a strong contribution in precipitation hardening. The long-term creep leads to coarsening of Laves-phase, and, thus, the distribution of Laves-phase must be controlled in order to improve the creep strength of 9-12% Cr martensitic steels.

Fig. 2.6 shows different precipitates typically formed in high Cr martensitic steels.
2.2 Metallurgy of 9-12% Cr martensitic steels

2.2.4 Design of 9-12% Cr martensitic steels. Influence of alloying elements

The influence of individual alloying element on creep resistance of martensitic steels is highly dependent on its quantity as well as the presence and quantity of other elements. Even a small difference in alloying contents may significantly change the mechanical properties of steels. However, all alloying elements may be classified based on their ability to form carbides [2].

Carbide forming elements: Cr, C, V, Nb, Ta, Ti.

Moreover, each alloying element plays its special role (sometimes several roles) in alloy design for martensitic steel.

Chromium

Chromium (Cr) is commonly added in advanced martensitic steels in the amount of 9% (or even more) for oxidation and corrosion resistance. Cr contributes little to the solid solution strengthening and highly to precipitate hardening forming Cr rich carbides ($M_7C_3$, $M_{23}C_6$) as well as nitrides ($M_2X$). Cr strongly promotes the formation of detrimental $\delta$-ferrite, which forms during normalization or remains undissolved when heating into austenite.

Tungsten and Molybdenum

Tungsten (W) and molybdenum (Mo) have similar behavior in martensitic steels. They play two essential roles: solid solution strengthening and Laves phase precipitation. The first one takes part after heat treatment of steel and during the beginning state of annealing and creep. Then, a large fraction of W and Mo atoms is removed from the martensitic matrix to precipitate Laves phase resulting in a decrease of solid solution strengthening. W diffusion in iron is slower than Mo diffusion, therefore, substitution of Mo atoms by W leads to slowing down dislocation recovery and Laves phase formation.

Nickel, Cobalt, Manganese

These elements are used with goal to ensure the lack of $\delta$-ferrite in steel. Ni and Co are found to increase toughness. Co little contributes to
solid solution strengthening. Recent investigations showed an increase in creep resistance when adding Co by means of provoking MX and M\textsubscript{23}C\textsubscript{6} nucleation and slowing down their coarsening rates. Also, Co decreases the diffusion coefficient of Cr at 600 °C up to 25 %. On the other hand, Ni promotes the M\textsubscript{6}C formation, and therefore, M\textsubscript{23}C\textsubscript{6} destabilization \[2, 16\].

**Copper**

Copper (Cu) has a low solubility in \(\alpha\)-Fe and precipitates as Cu particles. Also, Cu promotes the nucleation of other phases during creep and aging.

**Vanadium, Niobium, Tantalum, Titanium**

They are very strong carbide, nitride and carbonitride formers, which precipitate as MX-type particles. They play an important role in precipitation hardening. Ta and Nb are found to produce austenite grain refinement. Notwithstanding, Ti may form oxides in martensitic steels, and by this, reduce the creep ductility. In addition, V and Nb have a tendency to form detrimental Z-phase at the expense of fine MX precipitates during aging.

**Carbon and Nitrogen**

Carbon, Nitrogen (C, N) are interstitial elements, strong carbide, nitride and carbonitrides formers. They also have a tendency to form clusters and Cottrell atmospheres in martensitic steels.

**Silicon**

Silicon (Si) is found to improve the oxidation resistance and increase the Laves phase coarsening rate. An extensive addition of Si in martensitic steels promotes the formation of \(\delta\)-ferrite and \(\sigma\) phase as well as stabilizes low-melting phases, which in their turn lead to hot-cracking. Therefore, Si in such steels should be limited to a certain extent.
2.3 Creep fundamentals

Creep resistance is one of the most important properties for high-temperature materials, such as 9-12% Cr martensitic steels. Creep is generally defined as an irreversible plastic deformation of a material, which is subjected to a constant stress (load) below yield stress of the material, and an elevated temperature (> 0.4T_m), where T_m is an absolute melting temperature. Yield stress, \( \sigma_y \), of material is the stress, at which the material begins to deform plastically. In practical applications, it is often taken as the point where 0.2% plastic (irreversible) deformation occurs. Creep tests are conducted at constant loads and temperatures using creep machines equipped by furnaces, loads, thermocouples and control systems. The results of creep tests are graphically plotted as creep curves that represent time dependence on the strain or/and creep rate [4, 13] (Fig. 2.7).

Fig. 2.7 represents creep curves, which are normally drawn using experimentally obtained data (strain and time) along with their creep rate curves recalculated using the following equation:

\[
 s = d\varepsilon/d\tau, \quad (2.6)
\]

where \( \varepsilon \) is strain and \( \tau \) is time.

Creep curves are generally described as a three-stage-phenomenon including:

**Boron**

Addition of a small amount of boron (B) can significantly improve creep resistance of martensitic steels. B improves hardenability and decreases the coarsening rate of M_{23}C_6 precipitates. Some B atoms remain in solid solution and may form Cottrell atmospheres on dislocations. Addition of large amount of B can lead to the nucleation of coarse BN nitrides, which may degrade the creep strength. However, the role of B and its mechanisms of affecting the creep strength in martensitic steels has not yet been fully understood.

*To get deeper into the understanding of B behavior, the section 2.6 is dedicated to the mysterious element - B.*
• Primary (transient creep). At that stage (from $\varepsilon_0$ to $\varepsilon_1$) the creep rate decreases with time due to strength increase caused by hardening processes.

• Secondary (steady-state creep). At that stage (from $\varepsilon_1$ to $\varepsilon_2$) the creep rate is constant, which is associated with a balance between hardening and softening processes.

• Tertiary (accelerated creep). At that stage (from $\varepsilon_2$ to $\varepsilon_r$) the creep rate dramatically increases with time until rupture. Increased strain in the tertiary stage is a result of the necking and, therefore, enhanced stress, as well as the microstructure evolution of the material.

Duration and shape of all creep stages may vary depending on the nature of material and applied parameters ($T, \sigma$). Increases in $T$ and $\sigma$ lead to the reduced secondary stage of creep and decreased rupture time (Fig. 2.8). It is worth to notice that for 9-12% Cr martensitic steels, the secondary stage of creep is often absent and a minimum creep rate is to be estimated instead.

The aim of creep testing is to determine the creep strength of the material characterized by:

• Creep strain limit (a certain deformation during a certain time at a certain temperature).

• The minimum creep rate (or minimum deformation rate of a material subjected to a constant load and temperature).

• Ductility, ability of material to deform plastically before rupture (usually in order to estimate ductility either elongation or reduction in cross section of the test specimen should be measured).

• Time to rupture.

2.4 Creep strengthening and degradation mechanisms

The understanding of microstructure strengthening mechanisms is essential for designing a new generation steel and improving its creep strength.
2.4 Creep strengthening and degradation mechanisms

Figure 2.7: Creep curves constant load and temperature (a-b), and creep rate curves (c-d) as a function of time. $\varepsilon_0$ represents instantaneous strain, which consists of elastic strain and possibly plastic strain depending on the stress level [4].

Figure 2.8: Schematic creep curves varying with stress and temperature [4].
The strengthening of martensitic microstructure should be achieved during quality heat treatment and not be lost significantly during creep and aging. The creep strength is normally achieved by a complex of different strengthening mechanisms where it is difficult to determine the contribution of each mechanism. Creep strengthening mechanisms for martensitic steels include the ability to delay dislocation migration and subgrain growth at the elevated temperatures and pressures. The main strengthening mechanisms in martensitic steels are dislocation strengthening, solid solution hardening, and precipitation hardening [4, 14].

Dislocation hardening

Dislocations can act as obstacles for dislocation movement. Martensite microstructures are usually characterized by high dislocation density \(10^{14}–10^{15} \text{ m}^{-2}\), which produces the dislocation hardening at room temperature. The dislocation density obtained during the martensitic transformation is normally reduced by varying the tempering temperature. Dislocation hardening \(\sigma_{or}\) is given by:

\[
\sigma_{or} = 0.5MGb(p^f)^{1/2},
\]

(2.7)

where \(p^f\) is free dislocation density in matrix, \(M\) is Taylor factor (=3), \(G\) is shear modulus, \(b\) is Burgers vector.

However, the presence of high dislocation density in the martensitic steels can lead to the accelerated recovery and recrystallization processes at elevated temperatures. Therefore, the dislocation hardening has a strong effect only in the short term of creep and it is intensified by precipitation hardening when second phase particles pin free dislocations.

Solid solution hardening

When interstitial or substitutional atoms are added to the matrix of the martensitic steels, they introduce lattice distortions, which may impede dislocation movements. Substitutional atoms, such as W and Mo, are considered to be the main contributors to solid solution hardening in martensitic steels due to their relatively large size (much larger than the size of the solvent atom - Fe). It should be noted, that when Mo and
W rich precipitates, such as the Laves phase, form, they take Mo and W atoms out of the solid solution resulting in a reduction of the solid solution hardening effect.

**Precipitation hardening**

The precipitation hardening in martensitic steels is achieved by the formation of secondary phase particles (MX-type carbonitrides, $M_{23}C_6$, $M_6X$, Cu-precipitates, Laves phase and etc.) which serve as obstacles for dislocation movement. Depending on their locations in the microstructure (matrix or sub-boundaries), the precipitates may stabilize free dislocations or sub-grains against recovery, resulting in dislocation or sub-boundary hardening, respectively. The contribution of the precipitation hardening to the creep strength can be estimated by the Orowan equation:

$$\sigma_{or} = \frac{0.84MGb}{\lambda} = \frac{3.32Gb\sqrt{f_p}}{d_p},$$

(2.8)

where $M$ is Taylor factor (= 3), $G$ is shear modulus, $b$ is Burgers vector and $\lambda$ is the mean interparticle spacing, $f_p$ is the precipitate volume fraction and $d_p$ is the mean precipitate diameter.

Coarsening of secondary phase precipitates and transformation of fine MX carbonitrides into relatively coarse Z-phase particles are important degradation mechanisms, which increase the mean interparticle space and decrease the precipitation hardening.

**Sub-boundary strengthening**

Sub-boundary strengthening is based on the grain size effect on the capacity to deform. The deformation in materials occurs by dislocation movement and grain boundaries act as obstacles for the dislocation propagation. When applying stress, dislocations move until they face a GB with repulsive stress field, which impedes the dislocation movement to the adjacent grain. Their pile up at the Grain boundary (GB) generates high repulsive force reducing the GB energetic barrier for dislocation movement across the GB. Then, further deformation in the material occurs. However, the smaller grain size, the higher applied stresses are
necessary to cross the GB. This finding is described by the Hall-Petch relationship.

\[ \sigma_{0.2} = \sigma_0 + k_{0.2}/d^{1/2}, \] (2.9)

where \( \sigma_{0.2} \) is yield stress, \( \sigma_0 \) is material constant for the starting stress for dislocation movement, \( k_{0.2} \) is strengthening coefficient, \( d \) is average grain diameter.

From the above, a material is stronger if the grain size is smaller. In martensitic steels, microstructure is divided by laths and blocks, which can be regarded as elongated sub-grains. They provide sub-boundary strengthening:

\[ \sigma_{sg} = 10G\lambda_{sg}, \] (2.10)

where \( \sigma_{sg} \) is sub-grain stress, \( G \) is shear modulus, \( b \) is Burgers vector, \( \lambda_{sg} \) is martensite lath width.

**Microstructure degradation**

The coalescence of martensite laths and blocks during creep results in an increase of \( \lambda_{sg} \). To prevent this recovery, fine precipitates such as MX carbonitrides and \( M_23C_6 \) carbides should be formed along the boundaries during tempering. The GB precipitates stabilize martensite substructure preventing (or slowing down) the movement of sub-boundaries.

The stabilization of the martensite microstructure is a key to the high long-term creep strength during service. The evolution of the martensite microstructure of 9-12% Cr martensitic steels occurs with exposure time. Degradation mechanisms in such steels are associated with an increase of martensite packets, blocks and laths as well as the growth of secondary phase precipitates and nucleation of detrimental Z-phase by an expense of fine MX carbonitrides. Since precipitates pin sub-boundaries within the martensite microstructure, thus reducing the annihilation of dislocations and preventing the recrystallization process, their growth leads to the degradation of the dislocation structure and, therefore, to the martensite recovery. The evolution of secondary phase precipitates and dislocation structure during creep and aging as well as their effects on the martensite microstructure were documented for some 9-12% Cr martensitic steels [15]. Fig. 2.9 illustrates recovered
2.5 Thermodynamic modelling

As described the advanced martensitic steels contain a large number of alloying elements. It is highly useful to apply thermodynamic modeling to predict the amount and compositions of equilibrium phases formed in such steels. This is a highly useful tool for evaluation of alloy composition effects. A deep description of the details of this modeling method is out of the scope of the present thesis. It works by minimizing the free energy of alloy systems by incorporation of elements into various alloy phases, and it relies on databases describing the energy of individual elements and phases which may form. Various commercial software programs for thermodynamic calculations are available. Thermocalc ver. 2017b with the TCFE9 database was applied in the present work. Figure [2.10] shows an example of a calculation of equilibrium phases as a function of temperature for the martensitic 9% Cr steel P92.
2.6 Boron in steels

2.6.1 Nature of boron

It is known that size of a boron atom is larger than that of interstitial elements (C, N) and smaller than substitutional one (Fe, Cr, W) which leads to a large misfit between boron atoms and the steel lattice in both substitutional and interstitial sites. That makes boron suitable for both: substitutional and interstitial atoms [47, 48]. Such intermediate size of B atoms allows them to segregate onto lattice defects, phase interfaces and GBs. The dual nature of boron for long time was a source of controversy. Substitutional solid solution was detected by X-ray measurements while interstitial solid solution was observed using internal friction measurements [49, 50]. The presence of B in both substitutional and interstitial sites was also detected [51].

2.6.2 Segregation of boron on grain boundaries

The tendency of boron to segregate onto austenite grain boundaries is known since 1960s [52] when study of boron became possible once Particle tracking autoradiography (PTA) technique was invented. Since then, the segregation of B atoms onto GBs has been widely studied in austenite steels [53, 54, 55]. It was found that addition of less than 1
ppm of B in steel is sufficiently enough in order to observe boron segregation on GBs \[56\]. There are two main mechanisms by which boron atoms may segregate to GBs: equilibrium and non-equilibrium. The equilibrium segregation occurs when material is isothermal held at temperature sufficiently enough to allow the diffusion of solute atoms while non-equilibrium segregation occurs during cooling from high temperature by the solute atom-vacancy mechanism \[57, 58\]. It is generally accepted that amount of B atoms segregated onto an austenite GB is highly dependent on the holding temperature, cooling rate, character of GB, boron concentration in material, and the presence of other B-containing phases. In martensitic steels it is considered that boron segregates to PAGBs during normalization HT and then redistributes into martensite grains, often to \(\text{M}_{23}(\text{C,B})_6\) borocarbides during tempering HT \[59\].

### 2.6.3 Boron-added steels

It is known, all strong martensitic creep resistant steels developed so far consist of boron as an alloying element. The commercial fabrication of the B-added steels started as far back as World War II. However, due to limitations in the steelmaking process as well as lack of knowledge on B behaviour in steels from the research side, widespread production of such steels has not been implemented. One of the main issues at that time was keeping oxygen and nitrogen controlled during steel casting in order to prevent the formation of boron compounds. Since then, the steelmaking technology gradually improved allowing the control of boron in the steel matrix. The positive effect of B on creep strength of 9-12% Cr martensitic steels has been shown in recent projects in Japan, India, Europe, and Russia. A good example is Abe’s study of B content effect on creep strength (Fig. 2.10, \[10\]), where creep strength of the 9% Cr martensitic steel subjected to creep test at 650 °C under 80 MPa increases with increasing boron content up to 139 ppm. The evident strengthening effect of boron is dependent on steel composition and greatly pronounced in steels alloying with Mo, Ti and Nb. The positive effect of B on creep strength of P91 steel was shown by Das \[60\]. Recently, the strongest experimental steel alloyed with 30 ppm of B, which showed extremely high stability up to 40000 h at 650 °C under 120 MPa, was presented by Mishnev \[61\]. The strongest martensitic steels today used in advanced
power plants, P92 and FB2, are also alloyed with B. Some of the most outstanding B-added steels and their creep rupture test results are reported in Appendix A. Though very little information is available on B behavior in steels, it is clear that optimization of B content can lead to the further improvement of creep strength in high Cr martensitic steels.

2.6.4 Effect of boron on mechanical properties

Small additions of B markedly affect various mechanical properties of B-added steels, such as creep strength, hardenability, hot workability, toughness and tensile properties [60, 62, 63]. The beneficial boron effect on hardenability has been known since 1930s when B was added to unalloyed and low alloyed steels. Today B is considered as the strongest hardenability agent, which gives the same level of hardenability as other more expensive elements added in bigger quantity. Boron content for the maximum attended hardenability is found to lay at the range of 10 - 30 ppm. The theory proposed for mechanism by which B improves hardenability of numbers of steels consists of segregated onto PAGBs boron atoms or formed on PAGBs B-rich compounds. Migrated to PAGBs boron reduces the surface energy, thus, decreasing the driving force for ferrite nucleation. In addition, as it is shown in [63], the HT parameters also strongly influence the hardenability of B-added steels. Hot workability of B-added steels is observed to be highest at the boron
2.6 Boron in steels

content of 10 - 100 ppm. No clear mechanism describing boron effect on workability is available so far. Maximum tensile properties have been found for steel containing 60 - 80 ppm of boron, while a drop in Ultimate tensile strength (UTS) properties was observed right after increase in B content to 100 ppm.

2.6.5 Boron-containing precipitates

BN compound

Boronitrides (BN) usually precipitate in high Cr martensitic steels during solidification as big particles (about few-tens microns) if the contents of B and N are sufficiently high (Fig. 2.11). BN is a harmful phase since it removes the strengthening effect of B and N, reducing the fraction of MX carbonitrides and increasing the coarsening rate of $M_{23}C_6$ carbides, which in their turn lead to embrittlement of material as well as decrease in creep resistance [4, 64, 65, 66]. The levels of B and N should be optimized in order to avoid these precipitates. However, this approach requires the suppression of N down to approximately 100 ppm, which is difficult to carry out for large-scale air castings. Another method for removing detrimental BN particles lays in the austenitizing HT at high temperature (around 1200 °C) for 8-10 h, during which most of the BN boronitrides dissolve. Depending on a conducted HT (or mechanical HT), BN precipitates can form in different shapes [65]. Elongated shape of BN precipitates is often present in materials mechanically deformed, for instance, hot rolled.

$M_2B$ and $M_3B_2$ compounds

$M_2B$ and $M_3B_2$ are competitive phases containing the following metallic elements: Fe, Cr, and W. The $M_2B$ phase was observed to form in as-cast and as-rolled conditions of high Cr martensitic steels as big precipitates (few microns) (Fig 2.12) and have similar effect as BN boronitrides. $M_2B$ phase was found to dissolve at lower normalization temperature than BN phase (around 1150 °C) [65]. Both $M_2B$ and $M_3B_2$ precipitates have been identified in 12% Cr-Mo-V steels and austenitic steels containing high boron concentration (approximately 350-400 ppm in case of $M_2B$ and 40-100 ppm in case of $M_3B_2$ compounds) [67].
Figure 2.12: SEM picture of a BN precipitate (a). EDS spectrum obtained from the BN particle observed (b) [65].

Figure 2.13: SEM image of a $\text{M}_2\text{B}$ precipitate (a). EDS spectrum obtained from the $\text{M}_2\text{B}$ particle observed (b) [65].
2.6 Boron in steels

Figure 2.14: An APT reconstruction map from Cr$_{23}$(C,B)$_6$ located near a PAGB. The red dots are C atoms, the blue dots are B atoms [59].

Cr$_{23}$(C,B)$_6$ borocarbides

After tempering HT, only small amount of boron atoms remain in the martensitic matrix, most of them incorporate into Cr$_{23}$C$_6$ carbides forming Cr$_{23}$(C,B)$_6$ compound [30]. It was reported in number of publications about the positive effect of B particularly on the Cr$_{23}$C$_6$ precipitate refining and decreasing their coarsening rate. It is known that B segregates to the PAGBs during normalization and then diffuses back during tempering while Cr$_{23}$C$_6$ precipitates nucleate [68]. This fact explains the observation of B rich Cr$_{23}$(C,B)$_6$ precipitates in the vicinity of PAGBs and B-free Cr$_{23}$C$_6$ precipitates in the centers of the PAGBs. Therefore, precipitates formed closer to the PAGBs are supposed to consist of higher B concentration [30]. Liu et. al. presented Atom probe tomography (APT) observations of Cr$_{23}$(C,B)$_6$ precipitates in TAF steel and concluded that Cr$_{23}$(C,B)$_6$ located near the PAGBs consisted of approximately 2 at.% of B while ones located away from PAGBs - only 0.8 at.% of B (Fig. 2.14, [59]). M. Hättestrand and H.-O. Andrén also showed using APT that B is evenly distributed within individual Cr$_{23}$C$_6$ particle [69]. It was found that enrichment of boron in Cr$_{23}$C$_6$ carbides becomes more significant with increasing aging time. Asahi [70] reported that the addition of Mo to boron steel suppresses the precipitation of Cr$_{23}$(C,B)$_6$ borocarbide by retardation of carbon diffusion.

The following B rich precipitates were also identified: M$_3$B, MB, M$_3$B$_4$, MB$_4$, however, very little information on these borides in high
Cr steels is available [67].

2.6.6 Techniques used for detection boron atoms

There is very little information on boron in steels available in the literature caused by the technique limitations in detecting boron. The most common techniques enable boron identification are PTA, auger spectroscopy, Electron energy loss spectroscopy (EELS), Secondary ion mass spectroscopy (SIMS) (or NanoSIMS) and APT. Each technique has its advantages and disadvantages (cost, complexity, resolution, etc).

Using PTA and SIMS B was studied in austenitic steels on qualitative level [50, 54, 59]. These researches gave a valuable information about influence of HT parameters on the B distribution on GB. At that time it was determined that B segregates on austenite GBs during austenitizing HT and depending on the HT temperature and cooling rate the value of B segregation may be different. Later, with advert of NanoSIMS the B distribution was investigated in higher resolution not only in austenitic but also martensitic steels [59], particularly, the effect of tempering time on B segregation at GBs was studied. However, all mentioned above techniques could not give a quantitative information of B, which is essential for understanding mechanical properties of studied material, and difference in B segregation during various HTs was estimated by intensity of bright regions on the analysing maps representing B atoms.

Today, with advert of high-resolution EELS and Atom probe (AP) (or APT) techniques it became possible to provide with valuable knowledge on boron behaviour in steels via direct measuring B atoms in quantity attitude. Thus, some authors showed influence of other alloying elements, nature of GBs, and HT parameters on quantity of B segregations [68, 71, 72, 73]. Though all the advantages, the sample preparation for these advanced techniques (for detecting boron) requires being very accurate and complex, and still remains a bottle-neck of the techniques.

Bibliography


Chapter 3

Motivation and project objectives

As it is mentioned above, today high Cr martensitic steels are considered as advanced creep-resistant materials for thermal coal power plants. One of the most effective methods to improve their steam oxidation resistance through a proper alloy design instead of surface coatings is an increase of Cr content from 9% up to 11-12% \( [1] \). However, so far an optimal concept for microstructure design of 11-12% steels is not well-understood. All attempts to make stronger 11-12%Cr steels have been failed due to initiation of microstructure instabilities in numerous experimental steels caused by formation of Cr nitrides (Z-phase) \( [2, 3] \).

The present research explores a new alloying method for 11-12%Cr martensitic steels with stable microstructures, which is based on deep understanding and control of the underlying mechanisms causing the microstructure instabilities in previous 11-12%Cr steels.

Specifically, the aim of the project is a greater understanding the alloying concept for low nitrogen creep-resistant steels for application in fossil fuel power plants operating at ultra-supercritical steam parameters up to \( T=650\, ^\circ\mathrm{C} \) and \( p=320\, \text{bar} \). For this reason three core objectives were covered:

- microstructure characterization of low nitrogen alloys with increased Cr contents up to 11.5%;
  
  - examination of their microstructure and mechanical proper-
ties during tempering in comparison with known experimental low nitrogen steels;
– inspection of their ageing behaviour at elevated temperatures in comparison with known experimental low nitrogen steels;
– assessment of their creep behaviour and microstructure evolution during creep tests at elevated temperatures in comparison with known experimental low nitrogen steels.

• study of boron in creep-resistant steels as very little quantitative knowledge on this alloying element is available;
  – investigation of B segregation behaviour during normalization in martensitic steels with various B contents;
  – discovery of B-containing precipitates forming in martensitic steels with various B contents;
  – improving of experimental technique allowing the detection of B atoms.

• evaluation of alloying concept based on results obtained within the project for the further development of a stable high Cr martensitic steel.

Bibliography


Chapter 4

Experimental

4.1 Material and equipment used in the PhD project

In the current PhD project, 9-12% Cr martensitic steels were investigated; their chemical compositions are presented in Table 4.1. All studied steels are alloyed with reduced nitrogen and added boron; two of them (P92 and 100B) are industrial steels, others are experimental alloys. Belgorod alloy alloyed with 9% Cr was developed in Russia and included in the project as it shows a promising alloying design for improved creep resistance among advanced high Cr martensitic steels. B0 alloy was produced in Europe as a copy of Belgorod alloy for the further investigation of the mechanisms responsible for the high stability of steels alloyed by the present (low N - added B) concept. B1 alloy is a high Cr version (11.5% Cr) of this family of steels. SST 1/2/3 alloys with slightly different C and N contents were developed based on B1 steel with addition of Cu in order to additionally strengthen steel by Cu precipitation.

P92 (10 ppm of B) and 100B (108 ppm of B) together with B0 (72 ppm of B) alloys were used to study the boron behaviour in steels alloyed with various B contents.

Table 4.2 comprises the instruments used for experimental investigations in the present PhD project.
Table 4.1: The chemical compositions of the studied steels.

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<tr>
<th>Steel (w.%</th>
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4.2 Experimental techniques

Detailed investigation of materials microstructure is the basic action for understanding properties of materials and, therefore, establishing a correlation between their microstructures and properties. This knowledge allows controlling the microstructure behavior and material properties, and hence, the design of new improved materials. To fulfill this goal, Electron microscopy (EM) and Atom probe tomography (APT) are essential tools for modern researches.

The PhD project deals with topical issues in the field of high-temperature materials, which can be solved by deep understanding microstructure behavior of materials in nano scale. For this reason, advanced microscopy, and therefore, study of relevant techniques are required. This chapter consists of literature review on modern techniques used in the current PhD project.

4.2.1 Electron microscopy

Electron microscopy is the most useful and universal tool for exploring microstructures of different materials. The main advantage of EM over the Light optical microscopy (LOM) is higher resolution achieved by the lower wavelength of electrons. Another difference is that electrons are much stronger scattered by gases than light \[1\]. Increased interest in EM observed nowadays, is due to several factors. Firstly, the technique may be extended by the addition of a wide variety of supplements: low (down to –150 °C) and high (up to 1200 °C) temperatures, deformation characterization, X-ray spectra, scattered electrons and others. Secondly, a significant increase (1 Å or less) in resolution makes EM useful for direct imaging of crystal lattices. EMs are roughly divided into two main types: Scanning Electron Microscopes (Scanning electron microscopy (SEM)) and Transmission Electron Microscopes (Transmission electron microscopy (TEM)), however, there are some additional techniques existent, such as scanning mode in TEM and Transmission kikuchi diffraction (TKD), Electron backscatter diffraction (EBSD) in SEM which are highly used nowadays. TEM and SEM differ by image forming. Images in TEM are produced by electrons, which are transmitted through the investigated samples. It gives a high resolution and precise information on the internal microstructure
4.2 Experimental techniques

Figure 4.1: Electron — matter interactions: the different types of signals generated (a), interaction volume (b) [2].

of the investigated materials, such as Grain boundary (GB), precipitates, dislocations and even atom structure or lattice defects. While SEM images are formed by electrons, which are back-scattered from the surface (or near the surface) or generated in the surface (secondary electrons) of the samples [1]. All types of signals registered after the interaction between the incident electron beam and a specimen are shown in Fig. 4.1. Different signal types, used for imaging, chemical element mapping or quantitative characterization, occur due to change in direction and energy of incident electrons under such interaction; for example, secondary electrons are ejected after inelastic scattering meaning that the electron trajectory is only slightly changed, but their kinetic energy is lost due to interactions with the electrons in the atoms of a specimen, while backscattered electrons form when the electron trajectory is much changed, but the kinetic energy remains close to the one from incident beam (i.e. by elastic scattering events).

Each type of signals is generated from the different electron interaction volume (Fig. 4.1 (b)) and, therefore, has different image resolution; for example, Auger and secondary electron images are characterized by higher image resolutions than backscattered electrons or X-rays.

It should be taken into account when investigating specimens with a low melting point or volatile elements that electron beam excites lattice vibration and, therefore, heat can be produced, which may damage the material.
4.2.2 Transmission electron microscopy

Transmission electron microscopy (fig. 4.2) is a technique giving a point-to-point resolution of less than 0.2 nm, which permits the direct observation of sub atomic structure.

An electron beam transmits through an ultra-thin specimen, carrying the information about the structure of a sample. A typical TEM consists of an electron gun, a condenser, objective, projector lenses, apertures, a fluorescent screen, a pump system, a camera and a control system (Fig. 4.3). The electron gun, comprises a filament (usually V-shaped, made of LaB$_6$, or W), a Wehnelt cylinder and an anode that is located on the top of the microscope column. When applying high voltage electrons are emitted from the filament and accelerated towards the anode. Then, electrons are moving further through the hole in the anode and reach the condenser lenses, which allow controlling the area and intensity of the image. Between the condenser lenses, there is a condenser aperture responsible for the convergence angle. It is worth to notice, the size of the condenser aperture affects the quality and intensity of the image. Further below a specimen chamber is present. The TEM specimen (3 mm in diameter) is inserted by the special TEM holder between pole
4.2 Experimental techniques

Figure 4.3: Schematic illustration of TEM: construction (a), ray pass in image and diffraction modes (b) [7].

pieces of the objective lenses. The later are mainly used in order to form first intermediate or diffraction images. The next lenses called intermediate (or diffraction) can be switched between 2 modes: image and diffraction. In the image mode, they are focused on the image plane while in the diffraction mode – on the back focal plane. Between objective and intermediate lenses the objective aperture is located, which allows controlling the image contrast (to be inserted in the image mode). The final set of lenses are called projector lenses, they magnify the image (diffraction pattern) formed by objective lenses and visualize it onto the fluorescent screen [1, 5, 6].

4.2.3 Scanning electron microscopy

SEM produces images by scanning the surface with a focused beam of high-energy electrons, which interact with atoms at the surface of the samples (Fig. 4.4). A typical SEM requires an electron gun, similar to one in TEM, condenser and objective lenses, objective aperture, scanning coils, sample stage, control system, pumping system. The electron gun is placed on the top of a microscope chamber. Electrons are accel-
Figure 4.4: First practical SEM (a) [5], modern Nova NanoSEM 450 from FEI (b) [9].

ERATED TO THE ENERGY OF 1-30 keV (WHICH IS LOWER THAN THE ENERGY USED IN TEM 100-300 keV). THEN, THEY TRAVEL THROUGH THE CONDENSER AND OBJECTIVE LENSES, WHICH DEMAGNIFY THE ELECTRON BEAM, UNTIL THEY HIT THE SAMPLE (FINAL BEAM IS USUALLY 2-10 nm). SCANNING COILS DEFLCT THE ELECTRON BEAM, SO THAT IT SCANS THE SPECIMEN IN X AND Y DIRECTIONS RESULTING IN THE SURFACE IMAGING FORMED BY THE DIFFERENT ELECTRON DETECTORS (FIG. 4.5) [1].

SEM IS USED IN DIFFERENT MODES BASED ON SIGNALS FROM SECONDARY ELECTRONS, BACKSCATTERED ELECTRONS OR DIFFRACTED BACKSCATTERED ELECTRONS. SECONDARY ELECTRONS ARE USED FOR VIEWING OF IMAGES AND GIVE INFORMATION ABOUT MORPHOLOGY AND TOPOGRAPHY OF A SAMPLE, BACKSCATTERED ELECTRONS REVILED CONTRAST IN DIFFERENT PHASES BASED ON MEASURING ATOMIC NUMBER IN MULTIPHASE SAMPLES. DIFFRACTED BACKSCATTERED ELECTRONS ARE COMMONLY USED FOR GATHERING INFORMATION ON A CRYSTAL STRUCTURE AND ORIENTATION IN A SOLID CRYSTALLINE SAMPLE [1] [10]. EBSD IS A CHARACTERIZATION TECHNIQUE WHICH IS COMMONLY USED TO STUDY STRUCTURE, PHASE ORIENTATION, DEFECTS AND GRAIN MORPHOLOGY IN CRYSTALLINE OR POLYCRYSTALLINE MATERIALS. USUALLY, THE EBSD DETECTOR CONTAINS A PHOSPHOR SCREEN, COMPACT LENS, AND A COUPLE-CHARGED DEVICE (CCD) CAMERA. A SPECIMEN WITH A POLISHED AND EVEN SURFACE IS TO BE INSERTED IN THE SEM CHAMBER AND TILTED AT 70° TO THE DIFFRACTION CAMERA. THIS CONFIGURATION CAUSES INCREASED CONTRAST IN A DIFFRACTION PATTERN. THE ELECTRONS IMPINGE WITH THE SPECIMEN...
surface and thus interact with the atomic lattice planes. Some of such interactions satisfy the Bragg’s Law and undergo backscatter diffraction forming the diffraction patterns. The diffraction patterns are then to be individually identified using Miller indices. The image is generated on the phosphor screen and magnified by the compact lens, which in its turn focuses the image onto the CCD camera. Since the raw pattern is noisy, a background subtraction should be taken from several patterns and averaged. EBSD software analyses the diffraction patterns by measuring the positions of Kikuchi lines and their angles and compares to existent crystal structures from a database (Fig. 4.6) [1]. Recently, TKD in SEMs has been introduced for investigation of nanostructured materials where conventional EBSD is not applied due to the limited resolution. The main difference between EBSD and TKD is that the sample used for TKD is required to be electron transparent and mounted horizontally to the EBSD detector. Thus, the spatial resolution is improved down to 2 nm (mainly depending on investigated material). Standard EBSD software with slightly modified algorithms for indexing is to be used for analyzing the resulting diffraction patterns [13].
4.2.4 Energy-dispersive X-ray spectroscopy

Energy-dispersive X-ray spectroscopy is an analytical technique used for the elemental analysis of a sample. The Energy dispersive X-ray spectroscopy (EDS) system can be installed in both scanning and transmission EMs. Today EDS softwares allow to get point, line and map chemical analysis, intended for a variety of tasks. Figure 4.7a shows a typical point EDS spectra made from Titanium carbide using INCA software [14].

The EDS technique detects X-rays emitted from the sample during the bombardment by an electron beam. The physics of this process is shown in Fig 4.7b. The electron of the K inner shell is knocked out of an atom which in its turn becomes excited. To relax the atom, an electron from the L (M) outer shells jumps into the vacant position. The energy difference between K and L (M) shells is then emitted as characteristic X-rays with definite wavelength. The energies and wavelengths are different for different elements, and therefore, a chemical analysis can be performed by measuring them [1]. However, due to the low energies of such light elements as C, N, B, EDS is not powerful technique to use; in order to detect them, Electron energy loss spectroscopy (EELS) should be adopted instead.

4.2.5 Electron energy loss spectroscopy

Electron energy loss spectroscopy is also used for chemical analysis. When the electron beam passes through a specimen it excites electrons of
the specimen elements which may lead to a characteristic loss in energy. The amount of energy loss depends, in its turn, on the binding energy of electrons. By measuring different energy ranges chemical elements can be identified. An EEL spectrometer is mounted below a specimen and uses a magnetic field to deflect the electrons. Higher energetic electrons are less deflected. Eventually, the electron beam is to be dispersed into the energy spectrum (Fig. 4.8). The quantitative information can be gathered by analyzing the peak intensities of the spectrum. EELS is highly used for detecting light elements, which is a big advantage of this technique over the EDS [1].
4.3 Atom probe tomography

Atom probe tomography (APT) is one of the most advanced microscopes in use today and is of great interest for studying precipitates, GBs, phase transformations, surface and interface segregations. The reason for the high popularity of APT is in its ability to produce a three-dimensional, atomic-scale image, where each atom is identified. Figure 4.9 (b) represents the modern state-of-the-art instrument - the local electrode atom probe (LEAP). The atom probe combines a time-of-flight mass spectrometer and a point projection microscope. A high electric field (1010 V/m) is created on the apex of a sample, which is held at cryogenic temperatures, by applying a high voltage (10 kV) between the sample and a local electrode. In the LEAP a funnel-shaped aperture of the electrode is positioned near the apex of the sample (Fig. 4.10). Atoms from the sample apex are field evaporated as ions and accelerated toward the imaging detector. For chemistry identification of detected ions, the flight time of each ion is measured and, successively, the mass-to-charge ratio is calculated. The original position of atoms on the sample is determined by the hit position of the ions on a detector, meanwhile, the sequence of evaporation events is commonly used to obtain a depth coordinate.

The ability to accurately reconstruct original spatial positions of field-evaporated ions emitted from a surface is essential in the APT analysis. Understanding the evolution of tip shape and projection during
the field evaporation plays an important role when detailing the reconstructed needle. The reconstruction algorithms use a point-projection method. The Z increment is a simple function with respect to the detector impact position \((X, Y)\) and ion sequence \((Z)\) \cite{23}.

Despite that the APT is a unique instrument allowing to produce a three-dimensional atomic image, the number of users is still quite small due to the complexity of the instrument. In addition, APT requires an accurate sample preparation, and can provide information only on a small volume of material (up to 1 micron in length of analyzed volume) which does not meet the various research objectives. Recently, some constraints have been overcome with development of the Focus ion beam (FIB) and new 3DAP instruments which are easier in operating, however, sample preparation still remains the main bottleneck in various cases.

### 4.3.1 Sample preparation

Generally, APT tip must:

- be sharp and needle-shaped. An apex of a sample must have a
radius of between 10 and 150 nm during the whole APT experiment. Since the radius of the sample apex increases during the experiment due to a removal of atoms from the surface, a needle should be nicely sharpened with a starting radius of less than 50 nm [21].

- have a good electrical conductivity;
- be strong enough mechanically for significant evaporation;
- consist of a specific region of interest in a final sharp needle, preferably in the near-apex region (50-100 nm) [20].

There are two main methods for APT sample preparation existent nowadays. The first one, the method of electropolishing thin needles, is the most popular due to its simplicity and low cost. The method has traditionally been used to fabricate needles from metal wires, whiskers, or blanks, typically with dimensions of 0.25×0.25×10 mm$^3$ and known from the early APT investigations [23]. The second method, called focused ion beam milling (FIB), has been used for the fabrication of tips from site-specific regions of samples [24]. A disadvantage of focused ion milling is the formation of implanted layer of ions into the sample. Commercial instruments consist of gallium liquid-metal ion sources and used with accelerating voltages between 2 and 30 keV. Gallium implantation and ion mixing produce some artifacts in the specimen. However, for some specific tasks, the focused ion milling may be the only possible technique for sample preparation.

Next paragraph is dedicated to the detailed explanation of the FIB method, which was selected for the APT experiment in order to place a selected grain boundary in the investigated APT volume.

### 4.3.2 Focus ion beam

FIB instruments, which are often combined with scanning electron microscope facilities in dual-beam systems, permits, as was mentioned above, atomic-scale investigation of site-specific regions in numeral materials (e.g. precipitates, grain boundaries, or interphase interfaces) [20]. Generally, the FIB-based methods require a three-staged process. In the first stage, a blank of material is extracted from the region of interest.
Then, the blank is mounted on a support post (Si-coupon) with Pt or W deposition. Finally, the post with blank of material is sharpened into the needle-shaped specimen using a FIB technique progressively decreasing a current value and diameter of a sample [23].

The site-specific sample preparation requires an accurate placement of the feature of interest inside of an analyzed volume (Fig. 4.11). For the successful site-specific sample preparation, the implementation of the transmission Kikuchi diffraction technique is highly recommended.
Bibliography


Chapter 5

Results

5.1 Tempering behaviour of 11% Cr martensitic steels

In the current chapter, the microstructure behavior during tempering in the 11.1-11.4% Cr steels of SST1, SST2 and SST3 (Table 5.1) is described. SST alloys were normalized either at 1060 °C or 1100 °C for 1 h and tempered at the temperature region of 350 °C – 770 °C for 3 h. An interesting effect appearing after tempering at 650 °C has been revealed in the vicinity of PAGBs in the SST1/2/3 steels.

Table 5.1: The chemical compositions of the studied steels.

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<tr>
<th>Steel (w.%)</th>
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<td>1.68</td>
<td>1.60</td>
<td>1.56</td>
</tr>
<tr>
<td>B</td>
<td>0.008</td>
<td>0.007</td>
<td>0.0061</td>
</tr>
</tbody>
</table>
5.1.1 Light optical microscopy

The martensitic microstructures of SST steels after various HTs were verified by means of Light optical microscopy (LOM). Fig. 5.1 shows the martensite microstructures of SST1, SST2 and SST3 steels obtained by normalization from 1060 °C and 1100 °C, which are typical for high Cr martensitic steels [1-3]. In some pictures TiN precipitates are seen as square reddish particles. A small amount of δ-ferrite was observed only in the SST3 steel.

Figures 5.2 – 5.6 show the microstructures of SST1/2/3 alloys after tempering at various temperatures for 3 h. New microstructure feature located along the PAGBs was observed only after tempering at 650 °C. The effect seen as bright regions on LOM micrographs of the SST1 steel after normalization at 1060 °C and tempering at 650 °C is shown by green arrows in fig. 5.2. After normalization at increased normalization temperature of 1100 °C followed by tempering at 650 °C the effect is even more pronounced in the SST1 steel (Fig. 5.3). Similar tendency but more pronounced is observed in the SST2 steel where the effect on PAGBs appears only after normalization at 1100 °C and tempering at 650 °C while after normalization at 1060 °C followed by tempering at different temperatures (including 650 °C) it was not observed (Fig. 5.4, 5.5). Thus, increase in normalization temperature from 1060 °C to 1100 °C followed by tempering at 650 °C leads to the pronounced PAGB effect in the SST1 steel and to the appearance of the PAGB effect in the SST1 steel. However, in the SST3 steel this phenomena had not been found even after normalization at 1100 °C followed by tempering at 650 °C (Fig. 5.6). Therefore, not only tempering temperature but also normalization temperature should be considered during studying the influence of HT on the PAGB phenomena.

It should be reported that similar phenomena was observed in [4] in a 9% Cr martensitic steel after normalization at 1150 °C for 1 h followed by tempering at 780 °C for 4 h. However, no explanation of the microstructure specifically the PAGB phenomena, shown by LOM, was provided by authors.

In order to investigate the dependence of the PAGB effect on time of tempering, the SST3 steel, where PAGB phenomena was not found after normalization at 1100 °C and tempering at 650 °C for 3 h, was further held at 650 °C for longer time. After 8 h of holding at 650 °C the effect
Figure 5.1: LOM micrographs of SST1 (a, b), SST2 (c, d), and SST3 (e) subjected to normalization at 1060 °C for 1 h (a, c), and 1100 °C for 1 h (b, d, e).
Figure 5.2: LOM micrographs of the SST1 steel subjected to normalization at 1060 °C for 1 h and tempering at the temperature region of 350 °C - 770 °C for 3 h. Tempering temperatures are signed on the pictures.

Figure 5.3: LOM micrographs of the SST1 steel subjected to normalization at 1100 °C for 1 h and tempering at the temperature region of 350 °C - 770 °C for 3 h. Tempering temperatures are signed on the pictures.
5.1 Tempering behaviour of 11% Cr martensitic steels

**Figure 5.4:** LOM micrographs of the SST2 steel subjected to normalization at 1060 °C for 1 h and tempering at the temperature region of 350 °C - 770 °C for 3 h. Tempering temperatures are signed on the pictures.

**Figure 5.5:** LOM micrographs of the SST2 steel subjected to normalization at 1100 °C for 1 h and tempering at the temperature region of 350 °C - 770 °C for 3 h. Tempering temperatures are signed on the pictures.
**Figure 5.6:** LOM micrographs of the SST3 steel subjected to normalization at 1100 °C for 1 h and tempering at the temperature region of 350 °C - 770 °C for 3 h. Tempering temperatures are signed on the pictures.

**Figure 5.7:** LOM micrographs of the SST3 steel subjected to normalization at 1100 °C for 1 h and tempering at 650 °C for 3 h (a) and 8 h (b).
Figure 5.8: LOM micrographs of the SST1 steel subjected to normalization at 1100 °C for 1 h and tempering at 650 °C for time region of 0.2 h – 15 h. Tempering times are signed on the pictures.
Figure 5.9: LOM micrographs of the SST2 steel subjected to normalization at 1100 °C for 1 h and tempering at 650 °C for time region of 0.2 h – 15 h. Tempering times are signed on the pictures.
began to form on PAGBs in the SST3 steel (Fig. 5.7).

More detailed study of time dependence on the PAGB effect in the SST1 and the SST2 steels is shown in Fig. 5.8 and 5.9, respectively. The steels were subjected to normalization at 1100 °C for 1 h followed by tempering at 650 °C from 0.2 to 15 h. It is seen, that effect is visible from 1 to 5 h of tempering in the SST1 steel and from 30 min to 5 h of tempering in the SST2 steel and the effect is more significant in the SST2 steel.

5.1.2 Scanning electron microscopy

In order to understand the found PAGB phenomena deeper, EBSD analysis were performed in the SST1 and SST2 steels after normalization at 1100 °C and tempering at 650 °C for 3 h (Fig. 5.10). However, the microstructure observations had not revealed any features corresponding to the processes taking place at the PAGBs. The EBSD maps obtained on The SST1 and SST2 steels show typical martensitic microstructures not presenting any other phases or peculiar objects close to PAGBs.

Fig. 5.11 presents SEM images taken from the SST1 steel normalized at 1100 °C for 1 h and tempered at 650 °C for 3 h where the PAGB effect is clearly visible. The bright features in Fig. 5.11b correspond to secondary phase precipitates, mainly Cr-rich carbides. It is seen, that for some reason secondary phase precipitates nucleated within the matrix inside individual grains ending up about a 1 μm from the boundaries forming so-called precipitate denuded zones along the PAGBs. The width of these zones is estimated at approximately 2-3 μm (Fig. 5.11 c), which is far too wider than the width of GBs. The questions: why is it formed only during the tempering at 650 °C, whether the segregation of particular atoms takes place in the process of forming the denuded zones and how does it affect the properties and further steel behaviour during creep exposure at 650 °C, are not considered in the current project and left for the future investigations.

It should be noticed that PAGB effect was not observed at any tempering temperatures in the B0, B1, and Belgorod steels.
Figure 5.10: EBSD maps of the SST1 (a) and SST2 (b) steels subjected to normalization at 1100 °C for 1 h and tempering at 650 °C for 3 h.

Figure 5.11: SEM images of the SST1 steel subjected to normalization at 1100 °C for 1 h and tempering at 650 °C for 3 h.
5.1 Tempering behaviour of 11% Cr martensitic steels

Figure 5.12: Effect of tempering temperature on the hardness values of 10-12% Cr martensitic steels. Hardness values of Belgorod alloy were taken from [9].

5.1.3 Hardness

In Fig. 5.12 the hardness values of SST1 and SST2 steels normalized at 1060 °C and 1100 °C and tempered at various temperatures are shown along with hardness values of B0, B1 and Belgorod alloys normalized at 1060 °C and tempered at same temperatures as the SST1 and SST2 steels.

The hardness curves of all presented alloys have similar behavior. Hardness values are increasing from the tempering temperature of 350 °C until the tempering temperature of 525 °C where all steels are strengthened and after which they are rapidly softened at the tempering temperature range of 600 °C – 800 °C. Such hardness behavior is typical for 9-12% Cr martensitic steels. An increase of hardness in the range of 300 °C – 500 °C and a decrease of that in the range of 600 °C – 800 °C are generally attributed to the carbide reactions occurring at the different tempering temperatures. Figure 5.12 shows that the SST1 and SST2 steels are harder than the B0, B1 and Belgorod alloys, which can be explained by the presence of Cu in the SST1/2 alloys. It is known, that
Table 5.2: Hardness values of investigated steels measured after heating at different normalization and tempering temperatures.

<table>
<thead>
<tr>
<th>Tempering temperature, °C</th>
<th>Normalization temperature</th>
<th>SST1 1060 °C</th>
<th>SST1 1100 °C</th>
<th>SST2 1060 °C</th>
<th>SST2 1100 °C</th>
<th>B0 1060 °C</th>
<th>B1 1060 °C</th>
<th>Belgorod 1060 °C [9]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>463±5</td>
<td>468±4</td>
<td>480±2</td>
<td>538±5</td>
<td>399±11</td>
<td>454±3</td>
<td>387</td>
</tr>
<tr>
<td>20</td>
<td></td>
<td>435±5</td>
<td>446±2</td>
<td>449±15</td>
<td>438±12</td>
<td>397±4</td>
<td>433±4</td>
<td>396</td>
</tr>
<tr>
<td>350</td>
<td></td>
<td>467±4</td>
<td>475±2</td>
<td>481±5</td>
<td>467±9</td>
<td>347±7</td>
<td>449±3</td>
<td>387</td>
</tr>
<tr>
<td>450</td>
<td></td>
<td>477±4</td>
<td>490±3</td>
<td>508±10</td>
<td>487±12</td>
<td>413±3</td>
<td>472±3</td>
<td>394</td>
</tr>
<tr>
<td>525</td>
<td></td>
<td>477±4</td>
<td>490±3</td>
<td>508±10</td>
<td>487±12</td>
<td>413±3</td>
<td>472±3</td>
<td>374</td>
</tr>
<tr>
<td>550</td>
<td></td>
<td>316±4</td>
<td>343±1</td>
<td>322±4</td>
<td>346±3</td>
<td>285±3</td>
<td>295±1</td>
<td>278</td>
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<td>600</td>
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<td>268±2</td>
<td>267±2</td>
<td>276±2</td>
<td>274±2</td>
<td>230±5</td>
<td>249±2</td>
<td>235</td>
</tr>
<tr>
<td>650</td>
<td></td>
<td>268±2</td>
<td>267±2</td>
<td>276±2</td>
<td>274±2</td>
<td>230±5</td>
<td>249±2</td>
<td>235</td>
</tr>
<tr>
<td>700</td>
<td></td>
<td>268±2</td>
<td>267±2</td>
<td>276±2</td>
<td>274±2</td>
<td>230±5</td>
<td>249±2</td>
<td>235</td>
</tr>
<tr>
<td>750</td>
<td></td>
<td>268±2</td>
<td>267±2</td>
<td>276±2</td>
<td>274±2</td>
<td>230±5</td>
<td>249±2</td>
<td>235</td>
</tr>
<tr>
<td>760</td>
<td></td>
<td>263±1</td>
<td>255±3</td>
<td>256±3</td>
<td>267±2</td>
<td>223±1</td>
<td>242±3</td>
<td>201</td>
</tr>
</tbody>
</table>

Cu may form Cu-precipitates and, thus, improves strength of materials [5]. The SST2 steel has slightly higher hardness values compared to the SST1 one (Table 5.2), which is attributed to the higher C content in the SST2 steel.

5.1.4 Transmission electron microscopy

Tempered martensite lath microstructures not containing δ-ferrite or retained austenite were observed in the SST1/2 alloys after tempering at 750 °C. The PAG sizes in the SST1 and SST2 steels estimated by LOM are 57 µm and 52 µm, respectively, and the martensite lath widths are approximately 260 nm and 240 nm, respectively. The following particles were found in the as-tempered microstructures: MX carbonitrides enriched by Ti and Nb, Cr-rich M23C6 carbides and Cu-precipitates (Fig. 5.13). The average sizes of MX precipitates are approximately 45 nm and 53 nm in the SST1 and SST2 alloys, respectively, and the average sizes of M23C6 carbides are approximately 85 nm and 77 nm, respectively. It is worth to note that no V-rich MX carbonitrides were detected in these alloys. The presence of Cu-precipitates in the SST1 and SST2 alloys is revealed by holes on TEM thin foils. These holes results at electrochemical etching during the sample preparation leading to removal of Cu phase. EDS analyses of precipitates detached from the martensite matrix on carbon replicas using Cu grids were made only for identification of MX and M23C6 precipitates. The number fraction
5.1 Tempering behaviour of 11% Cr martensitic steels

Figure 5.13: TEM micrographs of SST1 (a, b, c) and SST2 (d, e, f) 11% Cr martensitic steels after tempering at 750 °C for 3 h: thin foils (a, d); carbon replicas (b, c, e, f).
of MX carbonitrides from the overall precipitates investigated by EDS using carbon replicas is only 2-3% in the SST steels after tempering. Other precipitates identified are Cr-rich M\textsubscript{23}C\textsubscript{6} carbides. As such, the microstructures of the SST1 and SST2 steels after tempering at 750 °C were rather similar.

5.1.5 Conclusion

11-11.5% Cr martensitic steels were investigated after normalization and tempering HT. The following conclusion is stated:

- All studied martensitic steels are characterized by a typical martensite microstructure decorated by secondary phase precipitates: Nb and Ti - rich MX type carbonitrides and Cr - rich carbides identified as M\textsubscript{23}C\textsubscript{6} after normalization from 1100 °C and temepering at 750 °C. Cu particles were indirectly observed on the martensite lath boundaries.

- Precipitate-demuded zones in the vicinity of PAGBs were observed after tempering at 650 °C, which were found to be sensitive to the applied temperature and time of tempering.

5.1.6 References


5.2 Microstructure evolution of 11% Cr martensitic steels during high temperature annealing and creep.

(in manuscript)

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aDepartment of Mechanical Engineering, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark

5.2.1 Abstract

Four experimental low nitrogen martensitic steels were investigated in order to study possibilities for development of 11-12% Cr martensitic steels with improved creep strength. Alloy design was made on basis of a previously developed low nitrogen 10% Cr steel, which had shown the best long-term creep stability at 650 °C. The microstructure evolution during annealing in the investigated steels was detailedy characterized using transmission electron microscopy. The creep strength of the investigated alloys did not reach the level of the 10% Cr steel most probably either because no fine nitrides precipitated or because fine nitrides transformed into Z-phase.

Keywords: high chromium martensitic steels, creep rupture stability, long-term ageing, precipitation behaviour, electron microscopy.

5.2.2 Introduction

9-12% martensitic steels are widely used as construction material for high temperature components such as rotors, turbines and pipes of steam power plants due to their excellent creep strength, corrosion and oxidation resistance in combination with relatively low cost [1, 2, 3, 4]. The creep properties of these steels limit the achievable steam pressure and temperature and there is thus a strong incentive to develop better steels to enable improved efficiency and reduced emissions from steam power plants.
In order to provide better 9-12% Cr martensitic steels new alloying concepts should be developed based on a deep understanding of the particular role of individual alloying elements in the microstructure degradation during creep.

The microstructure and, therefore, mechanical properties of 9-12% Cr martensitic steels is controlled by applying different heat treatments, which usually consists of normalizing from \(1050 \degree C\) - \(1150 \degree C\) to achieve a homogeneous martensite and tempering at \(720 \degree C\) - \(780 \degree C\) to soften the hard and brittle martensite as well as to precipitate second phase particles. The achieved tempered martensite microstructure consists of prior austenite grains (PAG), which are sub-divided into martensite blocks, packets and laths and contains a high density of free dislocations. Important precipitates include \(M_{23}C_6\) carbides ((Fe,Cr)\(_{23}\)C\(_6\)) located on PAG boundaries as well as on boundaries of martensite sub-elements and MX carbonitrides ((V,Nb,Ti)(C,N)) located on dislocations within the martensite matrix as well as on boundaries [5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15].

The stability of the martensite microstructure under creep loads is provided by several strengthening mechanisms including solid solution, precipitation, dislocation and sub-boundary hardening. During long-term ageing and creep the tempered martensite microstructure tends to degrade by mechanisms including subgrain growth and dislocation density decrease influenced by a gradual reduction of the precipitate hardening [16, 17, 18, 19, 20, 21, 22, 23, 24, 25]. The following changes in precipitates in 9-12% Cr martensitic steels have been observed to occur under creep conditions: coarsening of MX and \(M_{23}C_6\) carbides [5, 17, 18, 22, 27, 28, 29, 30, 31]; nucleation, growth and coarsening of Laves phase [3, 32, 33, 34, 35, 36], and formation of the relatively coarse Z-phase (Cr(V,Nb)N) at the expense of fine MX carbonitrides [37, 38, 39, 40, 41]. Further, a depletion of W and Mo atoms from solid solution takes place. In turn, these processes lead to creep strength breakdown.

The strongest creep resistant martensitic steels currently used in power plants are P92 (for steam pipework), FB2 (for large forgings) and CB2 (for castings) [42]. These steels contain 9%Cr and are able to work under supercritical steam parameters up to 300 bar and 610 \degree C. However, a desired temperature increase up to 650\degree C requires improved oxidation
5.2 Microstructure evolution of 11% Cr martensitic steels during high temperature annealing and creep.

resistance, which can be achieved by increased Cr content from 9 to 11-12%. Previous experimental alloys containing 11-12% of Cr as well as V, Nb and N for MX strengthening have been found to suffer from microstructure instability due to the formation of Z-phase, which is accelerated with increasing Cr content. Thus, new alloy concepts for high Cr martensitic creep resistant steels should focus on avoiding or delaying the Z-phase formation \[37, 42\]. Reduced nitrogen content to eliminate those nitrides, which lead to the formation of Z-phase during long-term creep and ageing, could be one way forward. A good example of such an alloy design is the Belgorod 10%Cr alloy with low N (≤0.003%) and added Ti, which has demonstrated the best creep strength at 650 °C among the 9-12% martensitic steels \[16, 22\]. Besides low N the Belgorod alloy has high content of B (≥0.007%) compared to previous grade steels.

The addition of only 20–150 ppm of B has been found to significantly improve creep strength of 9–12% martensitic steels. It is known that B incorporates into \(M_{23}(C,B)_6\) carbides during tempering, thus reducing their coarsening rate during creep. However, the mechanism of the reduced coarsening rate of \(M_{23}(C,B)_6\) is still not well-understood \[15, 43, 44, 45, 46, 47, 48, 49\].

In the present work we report about new 11.5% Cr-low N-B added martensitic steels, their alloying concept, microstructure stability and degradation under high temperature long-term creep and ageing.

5.2.3 Alloy design

The Belgorod alloy with 10% Cr has shown excellent creep stability up to 39,000 h at 650 °C/120 MPa \[16\]. It was developed in Russia based on the TOS 110 steel developed earlier by Thosiba in Japan and it includes reduced N and a small amount of Ti, Table 1. It was speculated that the Ti will tie up the nitrogen in the steel as TiN, which cannot transform to Z-phase, since this phase exists only in the variants CrVN, CrNbN and CrTaN and mixtures thereof \[50\]. The absence of Z-phase would explain the high microstructure stability of the Belgorod alloy. This could be a possible way to increase the Cr content and enable high oxidation resistance without compromising the long-term microstructure stability. Thus, a high Cr variant B1 of the Belgorod alloy was designed.
The creep results on the Belgorod steel had revealed a relatively high strain accumulation during primary creep as compared to other 9-12\% Cr martensitic steels \cite{16,22}, which could be due to the absence of fine nitrides. Cu is known to form fine precipitates in martensitic steels such as P122, but Cu precipitates coarsen relatively fast \cite{51}. Thus, two further experimental alloys SST1 and SST2 with addition of Cu for precipitate strengthening during short-term creep were designed.

A C++ program with access to Thermo-Calc ver. 2017b and the TCFE7.0 database was used \cite{52} to find an optimum balance between V, Nb, Ti, C and N which is expected to play a major role in the precipitation of fine particles providing precipitation strengthening. A large number of equilibrium calculations were made with systematic variation of the contents of these elements. Heat treatment effects were considered by first calculating the phase equilibria at the normalizing temperature and then using the calculated austenite phase composition to calculate the phase equilibria at tempering temperature. Fig. 5.14 shows the fraction and composition of MX precipitates formed during tempering versus the nitrogen content. According to the calculations, the fraction of MX precipitates increases and the type of MX changes from Nb rich to V rich precipitates with increase in nitrogen content.

Since it can be highly challenging to achieve very low nitrogen contents in steel making including air melting, a chemical composition with increased nitrogen content compared to the Belgorod alloy was targeted for the high Cr steel (SST2). The contents of V, Nb and Ti were bal-
5.2 Microstructure evolution of 11% Cr martensitic steels during high temperature annealing and creep.

anced to achieve similar MX behavior as for the Belgorod composition (B0). The increased N content, led to the necessity of sequential increases of Ti and Nb contents and decreased V content in order to avoid the formation of VN nitrides, which are expected to transform into Z-phase. Table 5.3 shows the target and real compositions of the studied steels.

Table 5.3: The chemical compositions of the studied steels. B0 target is the published composition for the Belgorod alloy [53] (mass %. Bal. Fe).

<table>
<thead>
<tr>
<th>Steel (w.%)</th>
<th>B0 target</th>
<th>B1 target</th>
<th>SST1 target</th>
<th>SST2 target</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.1</td>
<td>0.087</td>
<td>0.14</td>
<td>0.132</td>
</tr>
<tr>
<td>Si</td>
<td>0.06</td>
<td>0.07</td>
<td>0.06</td>
<td>0.08</td>
</tr>
<tr>
<td>Mn</td>
<td>0.1</td>
<td>0.13</td>
<td>0.12</td>
<td>0.12</td>
</tr>
<tr>
<td>Cr</td>
<td>10</td>
<td>10.03</td>
<td>11.5</td>
<td>11.47</td>
</tr>
<tr>
<td>Mo</td>
<td>0.7</td>
<td>0.71</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>W</td>
<td>2</td>
<td>2.02</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Co</td>
<td>3</td>
<td>2.8</td>
<td>3.5</td>
<td>3.51</td>
</tr>
<tr>
<td>Ni</td>
<td>0.17</td>
<td>0.18</td>
<td>0.17</td>
<td>0.18</td>
</tr>
<tr>
<td>Cu</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>0.008</td>
<td>0.0072</td>
<td>0.0085</td>
<td>0.009</td>
</tr>
<tr>
<td>N</td>
<td>0.003</td>
<td>0.0039</td>
<td>0.0045</td>
<td>0.0049</td>
</tr>
<tr>
<td>Ti</td>
<td>0.01</td>
<td>0.0145</td>
<td>0.017</td>
<td>0.028</td>
</tr>
<tr>
<td>V</td>
<td>0.2</td>
<td>0.2</td>
<td>0.12</td>
<td>0.12</td>
</tr>
<tr>
<td>Nb</td>
<td>0.05</td>
<td>0.053</td>
<td>0.055</td>
<td>0.056</td>
</tr>
</tbody>
</table>

5.2.4 Experimental

Four alloys were manufactured and tested. Besides the alloys B1, SST1 and SST2 mentioned above, the alloy B0 was made as a replica of the Belgorod steel for reference, Table 5.3. The differences between target and real values underline the challenges in steelmaking. The B0 and B1 were made by vacuum induction melting followed by rolling to 15 mm thick plate. SST1 and SST2 were made by air melting and vacuum arc re-melting followed by forging to 40 mm square bar.

The B0 and B1 steels were normalized at 1090 °C for 1 h, tempered at 780 °C for 2 h and air cooled to simulate steam pipe material. The SST1 and SST2 were heat treated to simulate a large forging, i.e. they were normalized at 1100 °C for 1 h followed by 2-step tempering including heating to 580 °C, holding for 2 h and air cooling; and heating to 750 °C, holding for 3 h and air cooling.

Annealing experiments were performed at 600 °C, 650 °C and 700 °C up to 10,000 h. The SST1 and SST2 steels were investigated more thor-
OUGHLY THAN THE B0 AND B1 STEELS. SPECIMENS WERE SECTIONED USING A STRUERS ACCUTOM SAW WITH AN ALUMINA DISK. MICROSTRUCTURES WERE INVESTIGATED WITH SCANNING AND TRANSMISSION ELECTRON MICROSCOPY (SEM AND TEM). A JEOL 2010 TEM EQUIPPED WITH AN INCA ENERGY DISPERSIVE X-RAY SPECTROSCOPE (EDS) WAS USED FOR STRUCTURAL CHARACTERIZATION OF MARTENSITE AND SECONDARY PHASE PRECIPITATES, WHICH WERE OBSERVED ON THIN FOILS AND CARBON REPLICAS, RESPECTIVELY. THIN FOILS WERE PREPARED BY DOUBLE-JET ELECTROPOLISHING IN A SOLUTION OF 10% PERCHLORIC ACID IN ETHANOL AT –35 °C AND 18-23 V USING ”TENUPOL-5”. SECONDARY PHASE PRECIPITATES WERE EXTRACTED ON CARBON REPLICAS USING CU-GRIDS AND QUORUM Q 150T ES COATING MACHINE. AT LEAST 150 RANDOM PRECIPITATES WERE IDENTIFIED IN EACH CONDITION OF AGEING BY MEANS OF EDS. A QUANTA 200 ESEM WAS USED FOR GENERAL MICROSTRUCTURE OBSERVATIONS. HARDNESS MEASUREMENTS WERE PERFORMED USING WOLPERT AND STRUERS DURASCAN 70 - G5 DEVICES UNDER THE LOAD OF 10 KG AT AMBIENT TEMPERATURE. LATH WIDTHS AND SECONDARY PHASE SIZES WERE MEASURED ON TEM MICROGRAPHS BY THE LINEAR INTERCEPT METHOD. CREEP TESTS WERE CARRIED OUT UNTIL RUPTURE AT THE 650 °C FOR ALL ALLOYS. IN ORDER TO COMPARE MICROSTRUCTURAL EVOLUTION DURING CREEP AND AGEING, A SAMPLE SUBJECTED TO CREEP (SST1 AT 120 MPa) WAS INVESTIGATED IN GRIP (WHERE CREEP DOES NOT TAKE PLACE) AND GAUGE (WHERE CREEP DOES TAKE PLACE) PORTIONS (Fig. 5.15).
5.2 Microstructure evolution of 11% Cr martensitic steels during high temperature annealing and creep.

5.2.5 Results

Initial microstructures

All investigated materials obtained after tempering showed tempered martensite lath microstructures with only minor content of δ-ferrite. The average PAG size was about 50 µm and the average martensite lath width was approximately 250 nm for SST alloys and 400 nm for B0 and B1 alloys. The following particles were found in the as-tempered microstructures: MX carbonitrides enriched by Ti and Nb and Cr rich M₂₃C₆ carbides. In addition, the SST1 and SST2 steels comprised Cu-precipitates, which were revealed by holes on TEM thin foils. These holes result from electrochemical etching during the sample preparation leading to the removal of Cu phase. EDS analyses of precipitates on carbon replicas using Cu grids were made only for MX and M₂₃C₆ precipitates. The number fraction of MX carbonitrides from the overall precipitates investigated by EDS on carbon replicas is only 2-3%. All other precipitates identified were Cr rich M₂₃C₆ carbides. It is worth to note that no V rich MX carbonitrides were detected in any of the alloys.

Annealing

Hardness values of SST1 and SST2 steels exposed to annealing at 600 °C, 650 °C and 700 °C up to 10,000 h are presented in Fig. 5.16. A slight decrease in hardness with annealing time can be observed in SST1 and SST2 steels aged at 600 °C and 650 °C. During annealing at 700 °C the hardness values of SST1 and SST2 steels significantly drop after 1,000 h of ageing. During short-term ageing the SST2 steel is harder than SST1, and then, during long-term ageing the SST2 hardness drops below SST1. However, after 5,000 h of ageing at 650 °C their hardness values become similar (235 HV) and with increasing ageing time up to 10,000 hours they both soften to 220-225 HV. The B0 and B1 steels show no indication of hardening similar to the SST2. They remain softer than the SST steels and soften parallel to the SST1 during annealing up to 10,000 hours at 650 °C.

Fig. 5.17 shows the evolution of the martensitic microstructure during annealing at 600 °C, 650 °C and 700 °C in the SST1 alloy. It is seen, that the microstructure remains martensitic up to 10,000 h of ageing.
Figure 5.16: Effect of annealing time and temperature on the hardness values of 11 %Cr martensitic steels.
5.2 Microstructure evolution of 11% Cr martensitic steels during high temperature annealing and creep.

Figure 5.17: TEM micrographs of martensite lath microstructure of SST1 steel exposed to annealing up to 10,000 h at 600 °C, 650 °C and 700 °C.
However, the microstructure parameters, such as martensite lath width and precipitate size, increase with increasing ageing time and temperature (Fig. 5.18, Table 5.4, Table 5.5). Thus, the average martensite lath width in SST1 steel after tempering is approximately 260 nm but after annealing at 650 °C for 5,000 h it increases to 350 nm and for 10,000 h the average martensite lath width reaches approximately 415 nm. Strong microstructure degradation is observed during annealing at 700 °C, where the average martensite lath width after 10,000 h of ageing grows to approximately 920 nm which is about 3 times higher than that after tempering (Fig. 5.18, Table 5.4). The traces of Cu precipitates (or round-shaped holes on TEM foils), indicate that Cu particles also grow with increasing annealing time and temperature. This tendency is much more significant during annealing at 700 °C, where the traces of Cu-precipitates are larger than during ageing at 600 °C and 650 °C (Fig. 5.17).

Similar tendencies of microstructure degradation are observed in the SST2 alloy but slightly faster (Fig. 5.19). Though the SST2 steel is more stable than SST1 steel during short time it becomes more degraded after 7,000 h of annealing and after 10,000 h of annealing at 650 °C. The average martensite lath width reaches approximately 440 nm while that in SST1 is approximately 415 nm (Table 5.4). At 700 °C of annealing after 10,000 h the microstructure of SST2 steel is partly recovered (Fig. 5.19).

Table 5.4: Evolution of martensite lath microstructure during annealing at different temperatures in 11% Cr martensitic steels.

<table>
<thead>
<tr>
<th>Annealing</th>
<th>Martensitic lath width, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>T, °C</td>
<td>0</td>
</tr>
<tr>
<td>SST1</td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>249±35</td>
</tr>
<tr>
<td>650</td>
<td>259±14</td>
</tr>
<tr>
<td>700</td>
<td>259±23</td>
</tr>
<tr>
<td>SST2</td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>256±56</td>
</tr>
<tr>
<td>650</td>
<td>232±38</td>
</tr>
<tr>
<td>700</td>
<td>303±34</td>
</tr>
</tbody>
</table>

Laves phase precipitates are detected already after 50 h of ageing with the mean size of 130 nm and after 10,000 h of ageing their mean size
5.2 Microstructure evolution of 11\% Cr martensitic steels during high temperature annealing and creep.

Figure 5.18: Effect of annealing time and temperature on the martensite lath size in 11\% Cr martensitic steels.

reaches 200 nm, which is lower than that in 9\%Cr martensitic steels [34, 49] and similar to one in Belgorod alloy [16]. The chemical compositions of Laves phase in the SST1 and SST2 steels are found to be similar. Further the formation of Z-phase was observed in the SST2 steel after 5,000 h of ageing while that was not found in the SST1 steel up to 10,000 h (Fig. 5.20).

The microstructures evolved in B0 (Fig. 5.21 a) and B1 (Fig. 5.21 b) steels after annealing at 650 °C for 1,000 h are fully martensitic and decorated by secondary phase precipitates. The martensite lath widths are larger than those in SST1/2 steels at the temperature region of 600 °C - 700 °C (Table 5.6) possibly due to the higher tempering temperatures. Particle sizes of M_{23}C_{6} carbides were significantly lower in the B0 and B1 steels as compared to the SST1 and SST2 steels and appeared to be more stable during ageing. The B0 and B1 showed similar stability of carbides as the Belgorod alloy [16]. The Laves phase particles in B0 evolve similar to the SST steels; whereas the B1 steel shows indication of slightly larger Laves phases, figure 5.22.

Fine precipitates in the B0 and B1 steels after ageing up to 10,000 h at 650 °C included very few Ti rich MX particles as well as one V rich MX particle found in the B0 steel, figure 5.23.
Figure 5.19: TEM micrographs of martensite lath microstructure of SST2 steel exposed to annealing up to 10,000 h at 600 °C, 650 °C and 700 °C.
5.2 Microstructure evolution of 11% Cr martensitic steels during high temperature annealing and creep.

**Figure 5.20:** TEM micrographs from carbon replicas taken after annealing at 650 °C for 10,000 h in: SST1 (a); SST2 (b) steels. The inset in (b) is EDS from Z-phase. The chemical compositions of all precipitates are given in at.%. 

**Table 5.5:** Evolution of secondary phase precipitates during annealing at 650 °C in 11% Cr martensitic steels. *N is number of precipitates identified and measured.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Tempered</th>
<th>Annealing at 650 °C</th>
<th>50 h</th>
<th>500 h</th>
<th>1000 h</th>
<th>5000 h</th>
<th>7000 h</th>
<th>10000 h</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MX, nm (N&lt;sup&gt;+&lt;/sup&gt;)</td>
<td>SST1</td>
<td>45 (2)</td>
<td>75 (2)</td>
<td>not found</td>
<td>58 (1)</td>
<td>72 (1)</td>
<td>64 (2)</td>
<td>87 (3)</td>
</tr>
<tr>
<td></td>
<td>SST2</td>
<td>53 (3)</td>
<td>84  (1)</td>
<td>not found</td>
<td>61  (1)</td>
<td>63 (1)</td>
<td>85 (2)</td>
<td>81 (2)</td>
</tr>
<tr>
<td>Cr&lt;sub&gt;23&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;, nm (N&lt;sup&gt;+&lt;/sup&gt;)</td>
<td>SST1</td>
<td>85±28 (108)</td>
<td>89±27 (67)</td>
<td>96±20 (116)</td>
<td>100±22 (140)</td>
<td>108±27 (84)</td>
<td>112±36 (120)</td>
<td>111±30 (157)</td>
</tr>
<tr>
<td></td>
<td>SST2</td>
<td>77±24 (87)</td>
<td>107±28 (94)</td>
<td>88±17 (102)</td>
<td>109±36 (117)</td>
<td>106±25 (58)</td>
<td>102±42 (158)</td>
<td>123±35 (118)</td>
</tr>
<tr>
<td>Laves phase, nm (N&lt;sup&gt;+&lt;/sup&gt;)</td>
<td>SST1</td>
<td>-</td>
<td>121±34 (21)</td>
<td>167±46 (28)</td>
<td>175±38 (24)</td>
<td>214±56 (25)</td>
<td>221±44 (22)</td>
<td>229±55 (26)</td>
</tr>
<tr>
<td></td>
<td>SST2</td>
<td>-</td>
<td>141±35 (24)</td>
<td>148±47 (26)</td>
<td>188±53 (31)</td>
<td>193±67 (22)</td>
<td>191±80 (14)</td>
<td>198±68 (18)</td>
</tr>
<tr>
<td>Z phase, nm (N&lt;sup&gt;+&lt;/sup&gt;)</td>
<td>SST1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>SST2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>166±85 (2)</td>
<td>not found</td>
<td>160±89 (3)</td>
</tr>
<tr>
<td>all precipitates, nm (N&lt;sup&gt;+&lt;/sup&gt;)</td>
<td>SST1</td>
<td>71±23 (160)</td>
<td>108±28 (216)</td>
<td>124±26 (164)</td>
<td>107±36 (200)</td>
<td>130±57 (170)</td>
<td>125±72 (164)</td>
<td>127±63 (202)</td>
</tr>
<tr>
<td></td>
<td>SST2</td>
<td>69±20 (117)</td>
<td>114±26 (146)</td>
<td>101±21 (154)</td>
<td>123±41 (168)</td>
<td>122±51 (123)</td>
<td>114±84 (222)</td>
<td>128±92 (160)</td>
</tr>
</tbody>
</table>
Figure 5.21: TEM micrographs of martensite lath microstructure of B0 (a) and B1 (b) steels exposed to annealing at 650 °C for 1000 h.

Table 5.6: Evolution of martensite lath microstructure during short-term annealing at different temperatures in 9-12% Cr martensitic steels.

<table>
<thead>
<tr>
<th>Ageing time, h</th>
<th>Steel</th>
<th>After tempering</th>
<th>Aging at 600 °C</th>
<th>Aging at 650 °C</th>
<th>Aging at 700 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average lath</td>
<td>1000</td>
<td>SST1</td>
<td>257±57</td>
<td>281±56</td>
<td>340±18</td>
</tr>
<tr>
<td>width nm</td>
<td>1000</td>
<td>SST2</td>
<td>237±34</td>
<td>275±66</td>
<td>284±49</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B0</td>
<td>407±20</td>
<td>522±72</td>
<td>564±101</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B1</td>
<td>361±42</td>
<td>390±57</td>
<td>453±51</td>
</tr>
</tbody>
</table>
5.2 Microstructure evolution of 11% Cr martensitic steels during high temperature annealing and creep.

Figure 5.22: Growth kinetics of secondary phase precipitates in number of 9-12%Cr martensitic steels during annealing at 650 °C. Particle sizes in Belgorod alloy were taken from [16].

Creep

Figure 5.24 shows creep rupture test results at 650 °C for the investigated steels in comparison with the Belgorod alloy [16]. As seen, during short term creep up to 1,000 h the creep resistance of SST2 steel is higher than that of SST1 steel. Then after about 3,000 h of creep SST2 steel degrades and SST1 steel has slightly higher creep strength than the SST2 steel. The creep rupture times of the B0 and B1 steels are much lower than the SST steels. However, the Belgorod steel shows much more stable creep behavior. The creep strength of SST1/2 steels at stresses of 140 MPa and 160 MPa is better, but at 120 MPa the time to rupture of Belgorod steel is approximately 7 times higher than that of SST1 steel.

Microstructure evolution during creep

Figure 5.25 shows the microstructure of SST1 steel ruptured after 5,392 h at 120 MPa and 650 °C in grip (a) and gauge (b, c) portions. It was found that creep strongly accelerates the degradation of the martensite
Figure 5.23: TEM micrographs from carbon replicas taken after ageing at 650 °C for 10,000 h in B0 (a) and B1 (b) steels. The chemical compositions of all precipitates are given in at.%. 

Figure 5.24: Time to rupture vs applied stress curves of SST1 and SST2 steels in comparison with B0, B1 and Belgorod alloys. Creep values of Belgorod alloy were taken from [16].
5.2 Microstructure evolution of 11% Cr martensitic steels during high temperature annealing and creep.

![TEM micrographs of the SST1 steel after creep test at 650 °C for 5392 h: grip (a), gauge (b,c) portions.](image)

Figure 5.25: TEM micrographs of the SST1 steel after creep test at 650 °C for 5392 h: grip (a), gauge (b,c) portions.

lath structure. The average martensite lath width in the grip section is approximately 420 nm, which is a bit higher than that found in the sample aged for 5,000 h where the average lath width was approximately 350 nm. The local strain in the sampled region of the gauge length was estimated at 9-13% based on sample diameter measurements. The microstructure in the gauge section shows great variation. In some areas the martensite lath structure remains with an average lath width of approximately 1.1 μm (Fig. 5.25 b), whereas in other areas complete recovery took place (Fig. 5.25 c). The average subgrain width in the recovered regions was estimated at > 3 μm.

Table 5.7 summarizes the microstructural parameters of the SST1 steel exposed to creep at 650 °C for 5,392 h up to rupture along with those of the SST1 steel aged for 5,000 h at 650 °C. Precipitates show 20% higher growth in the gauge section as compared to the grip section. In addition, one precipitate of Z-phase with size of 175 nm was detected in the gauge section of the creep sample of the SST1 steel while this phase was not observed during ageing up to 10,000 h (Fig. 5.26, Table 5.5).

5.2.6 Discussion

Four experimental alloys were investigated to explore possibilities to obtain high creep strength and microstructure stability in martensitic steels with 11-12% Cr, which could provide high oxidation resistance up to 650 °C. Their basic alloy concept was to reduce the nitrogen content and tie up remaining nitrogen as TiN to suppress the formation
Figure 5.26: TEM micrographs from carbon replicas taken after creep test at 650°C for 5,392 h in SST1 steel: in grip (a) and gauge (b) portions. The chemical compositions of all precipitates are given in at.%.

Table 5.7: Structural parameters of the SST1 11% Cr martensitic steel after creep and ageing at 650 °C.

<table>
<thead>
<tr>
<th>SST1</th>
<th>Martensite lath width, nm</th>
<th>MX, nm (N°)</th>
<th>Cr$_{23}$C$_6$, nm (N°)</th>
<th>Laves phase, nm (N°)</th>
<th>Z-phase, nm (N°)</th>
<th>all precipitates, nm (N°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aged sample</td>
<td>345±58</td>
<td>72 (1)</td>
<td>108±27 (84)</td>
<td>214±56 (25)</td>
<td>-</td>
<td>130±57 (170)</td>
</tr>
<tr>
<td>Creep sample</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(5392 h) grip</td>
<td>420±108</td>
<td>not found</td>
<td>102±24 (88)</td>
<td>193±57 (23)</td>
<td>-</td>
<td>119±31 (142)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1100±197</td>
<td>124±31 (64)</td>
<td>214±52 (41)</td>
<td>173 (1) 163±43 (225)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>/ &gt; 3 μm</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
5.2 Microstructure evolution of 11% Cr martensitic steels during high temperature annealing and creep.

of MX nitrides based on V or Nb, which would transform into Z-phase \((\text{Cr}(\text{V},\text{Nb})\text{N})\) accelerated by increased Cr content. All experimental alloys had similar contents of boron (70-90 ppm) to provide high coarsening stability of \(\text{M}_{23}(\text{C,B})_{6}\) carbides.

The first alloy B0 was made to replicate the published composition of the low nitrogen 10% Cr Belgorod alloy, which had shown superior long-term creep stability at 650 °C. The second alloy B1 was a high Cr version of the B0 and two further alloys SST1 and SST2 were made with Cu additions to provide short-term precipitate strengthening. The specified alloy compositions contained balanced additions of C, Ti, Nb, V and N to avoid the formation of vanadium rich nitrides after tempering. The SST alloys had increased nitrogen contents achievable in steelmaking which included air melting.

As seen in figure 5.24, none of the manufactured alloys could achieve the high creep stability observed for the Belgorod alloy. Even the B0 alloy, which was made as a replica of the Belgorod alloy had much poorer creep strength. In the following we provide possible explanations for the differences in creep strength and microstructure stability.

**Phase equilibria calculations**

Thermocalc calculations of fine precipitates for the achieved compositions of the manufactured steels compared to the target compositions are shown in figure 5.27. Calculations were made at the actual tempering temperatures for the steels and at 650 °C using the compositions of the austenitic matrix at the actual normalizing temperatures, i.e. the precipitates, which were undissolved at the normalizing were removed from the further calculations. Z-phase was suspended from the calculations at tempering temperature, whereas it was allowed to form at 650 °C. The TiX phases were mainly TiN, the NbX phases were mainly NbC and the VX phases were mainly VN.

It has recently become clear that the originally published Ti content of 0.01 wt% for the Belgorod alloy was probably inaccurate. Later published compositions for the steel indicated a significantly lower Ti content of 0.002 wt% [16]. Other elements are similar to the B0 target composition. Since this could have significant influence on the steel behavior, the Belgorod 2018 composition with 0.002 wt% Ti was included in the calculations, figure 5.27.
It is seen that the intention to avoid VN formation after tempering was achieved for the manufactured compositions of the B0 and B1 steels, but not for the SST1 and SST2 steels. Also it is found that the Belgorod 2018 alloy is not predicted to be free of VN in the as-tempered condition.

All alloys are predicted to form Z-phase during exposure at 650 °C; however the steels with predicted VN content form the highest amount of Z-phase according to the calculations.

The calculations for manufactured compositions indicate that similar amounts of Laves phase (2 vol.%) should form in all alloys during exposure at 650 °C. The amount of M$_{23}$C$_6$ carbides are predicted at: B0: 1.6 vol.%; B1: 2.5 vol.%; SST1: 2.5 vol.%; SST2: 3 vol.% and Belgorod 2018: 1.9 vol.%. Finally, the SST1 and SST2 steels should form 1.2 vol.% of Cu precipitates.

**Microstructure evolution**

The lath width shows strong correlation with hardness of the steels. The SST steels tempered at 750 °C show finer lath size and higher hardness than the B0 and B1 steels tempered at 780 °C. The lath size of the Belgorod steel after tempering is similar to the B0 and B1 steels [16]. The hardness of the steels B0, B1, SST1 and SST2 steels show a parallel decrease between 5,000 and 10,000 hours of ageing at 650 °C. Only the
5.2 Microstructure evolution of 11% Cr martensitic steels during high temperature annealing and creep.

SST2 steel shows indication of secondary hardening up to 3,000 hours of ageing and then the hardness drops significantly between 3,000 and 5,000 hours of ageing.

The precipitates are assumed to provide the stability of the tempered martensite at high temperature by precipitation hardening. The particle strengthening scales with:

$$\frac{\sqrt{f}}{d}, \quad (5.1)$$

where $f$ is the volume fraction and $d$ is the mean particle size.

The precipitates found in the largest amount in the steels are the M$_{23}$C$_6$ carbides, the Laves phases and the Cu precipitates (indirectly found). The M$_{23}$C$_6$ carbides in the SST steels are generally larger than in the B0, B1 and the Belgorod steels, but according to the equilibrium calculations their volume fractions are also larger. According to equation 5.1, the particle hardening from M$_{23}$C$_6$ carbides is 1.3% larger in the SST2 steel as compared to the B0 steel after 3,000 hours of ageing at 650 °C. The size evolution of M$_{23}$C$_6$ carbides in the B0 steel is slower than in the SST2 steel but their particle hardening is only 5% smaller in SST2 than in B0 after 10,000 hours of ageing at 650 °C. The coarsening stability of M$_{23}$C$_6$ carbides is similar in the B0 and Belgorod alloys. The large difference observed in microstructure stability and creep strength of the investigated steels indicate that the stability of the M$_{23}$C$_6$ carbides is not the most important factor for the microstructure stability of the investigated steels.

The Laves phase evolution is rather similar in all steels and due to their large particle size they only provide limited particle strengthening. Thus, the Laves phases do not offer a good explanation for the observed large differences in strength and microstructure stability.

The Cu particles in the SST steels are assumed to provide short-term strengthening only, since their coarsening stability is low. Together with the lower tempering temperatures the Cu particles precipitation hardening from Cu could provide an explanation for the improved short-term creep strength as compared to the Belgorod steel.

Observed MX precipitates in all of the steels include Nb or Ti rich particles, but since they are only observed in very small numbers and in sizes, which are of the same order as the M$_{23}$C$_6$ carbides they are not
expected to contribute significantly to precipitation strengthening.

When we look at the calculations for MX precipitates in the steels after tempering using the manufactured compositions, a possible explanation for the observed differences in microstructure stability lies in the “free” nitrogen, which is predicted to form VN precipitates. The steels Belgorod 2018, SST1 and SST2 are the strongest steels, and the only steels which should form VN after tempering. The B0 and Belgorod 2018 steels show very similar carbide stability and microstructure evolution, but the B0 is much weaker than the Belgorod steel in creep, and it has no possibility to form VN particles.

Very fine VN particles with sizes of 5-15 nm have previously been observed by atom probe tomography in a 10%Cr steel with high boron content and high creep strength [29]. It is possible that such fine VN could precipitate in the Belgorod and SST steels during creep, since they cannot be observed with the microscopic techniques applied in the present investigations. According to equation 5.1 precipitate hardening from VN with a volume fraction of 0.01% and a particle size of 10 nm is six times higher than the precipitate hardening from $\text{M}_2\text{C}_6$ carbides.

The observations of Z-phase particles in the SST2 steel after ageing and in the SST1 steel after creep support the hypothesis of fine VN precipitates. Fedoseeva et al. [39] showed that creep strain strongly promotes the transformation of V rich MX carbonitrides into Z-phase in a 9% Cr martensitic steel. Z-phase of similar sizes as in the SST steels were also observed in the Belgorod steel after long-term creep [16].

The difference in creep stability between the SST1, SST2 and the Belgorod alloy can then be explained by higher Cr content in the SST steels, which accelerate the Z-phase formation [37].

5.2.7 Summary

In the present work four 10-11.5% Cr martensitic steels with low N and added Ti and B were investigated during long-term ageing and creep. The investigations showed:

- Slight differences in Ti and N contents in steels lead to strong differences in creep strength: The steels where no free nitrogen is available after TiN formation showed much poorer creep strength than steels where free N is available.
• Cu particles improve strength of steels with 11.2% Cr and low nitrogen during short-term creep.

• Thermodynamic calculations indicate that free nitrogen could lead to the formation of VN nitrides, which could transform to Z-phase.

• The 11.2% Cr steel with the highest amount of predicted VN phase showed Z-phase formation after 5000 h at 650 °C while the 11.2% Cr steel with lower predicted VN showed no Z-phase formation up to 10000 h of ageing, but accelerated Z-phase formation was observed after 5000 h of creep.

• The difference in creep stability between 10% Cr and 11.2% Cr steels with free nitrogen is attributed to the higher Cr content, which accelerates Z-phase formation.

It is speculated that extremely small VN precipitates (5-15 nm), which strongly contribute to stable precipitation hardening, could explain the high creep stability of the 10% Cr steel with free nitrogen. Such fine VN precipitates were not found using TEM in the present steels but they should be chased by high-resolution techniques in future.

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Bibliography


5.3 Boron behaviour in 9-10% Cr martensitic steels

(in manuscript)

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Abstract

The boron behavior during normalization at 1100 °C for 1 h and air cooling was investigated in three 9-10% Cr martensitic steels containing 10, 72 and 108 ppm of boron. Atom probe tomography (APT) showed that boron segregates to austenite grain boundaries (AGBs) during cooling. The detected profiles did not allow determining whether diffusion limited equilibrium or non-equilibrium segregation prevails as segregation mechanism. Boron segregation at AGBs seems to saturate at 0.8 at.% in 9-10% Cr martensitic steels. >100 ppm boron leads to formation of fine M\textsubscript{2}B borides on AGBs during cooling. A large proportion of the added boron does not segregate, and some of the added boron form large BN particles during solidification or cooling.

\textit{Keywords: Atom probe, Boron, Segregation, Prior austenite grain boundaries, Steel, Martensite.}

5.3.1 Introduction

Modern martensitic 9-12% Cr creep resistant steels, such as Grades 91 and 92 for steam pipes and FB2 and CB2 for turbines have been recently developed for improved thermal efficiency of steam power plants. Their creep properties enable operation at elevated steam temperatures up to 600-620 °C, and there is a strong request for further improved steels of this class in order to reduce emissions from thermal power plants \cite{1,2}. 
The microstructure of the 9-12% Cr steels is tempered martensite formed during a final heat treatment, which usually consists of normalizing from 1050 °C - 1150 °C to achieve a homogeneous martensite and tempering at 720 °C - 780 °C to soften the hard and brittle martensite as well as to precipitate second phase particles. The achieved tempered martensite microstructure consists of prior austenite grains (PAG), which are sub-divided into martensite blocks, packets and laths and contains a high density of free dislocations. The long-term microstructure stability is based on solid solution strengthening from elements such as Mo and W as well as precipitation strengthening from mainly M$_2$C$_6$ carbides and fine (V,Nb)(C,N) carbonitrides [3, 4].

The chemical compositions of the modern 9-12% Cr steels have reached a high level of complexity, and thus, further improvements require alloying concepts, which must be based on a deep understanding of the role of each individual element, its behavior and effect on creep strength. In the present work we focus on the behavior of boron in 9-10% Cr martensitic steels.

It was found that addition of only 20-150 ppm of boron to 9-12% Cr martensitic steels can improve their creep strength substantially [5]. The positive effect of boron on the mechanical properties is used in commercial steels like the P92, FB2 and CB2 as well as in a number of promising experimental alloys [6, 7, 8, 9]. It was recently found that the addition of 80 ppm B together with reduced N down to 30 ppm strongly improved the creep strength of a 10%CrMoW steel [10, 11]. There is, however, a lack of detailed understanding of boron behavior in such steels.

**Boron behaviour**

Boron has an intermediate atom size, which is larger than the interstitial steel alloying elements (e.g. C and N) and smaller than the substitutional ones (e.g. Cr, Mo and W) [12]. This means that in bcc-iron boron is located in both substitutional and interstitial sites [13, 14, 15], and it gives boron a high tendency to segregate to lattice defects, phase interfaces and grain boundaries (GBs). In martensitic 9-12% Cr steels boron segregates to austenite GBs during normalization and during tempering it redistributes into martensite grains and is incorporated into precipitating boro-carbides of M$_{23}$(C,B)$_6$-type [16]. The coarsening rate
of $M_{23}(C,B)_6$ is reduced compared to $M_{23}C_6$ carbides in boron free 9-12% Cr steels and this is often seen as the key mechanism to enhance the microstructure stability and creep strength of boron alloyed 9-12% Cr martensitic steels. However, the mechanism for the detected reduction in the coarsening rate of $M_{23}(C,B)_6$ carbides still remains unclear [17, 18].

Boron in 9-12% Cr martensitic steels may also precipitate as boride phases, such as $M_2B$ and $M_3B_2$, where M is mainly Fe, Cr, Mo and W. Such borides are most often found as large precipitates formed during solidification. This may result in reduced toughness as well as depletion of boron from the steel matrix, which reduces its strength enhancement. Boron additions to the 9-12% Cr steels are normally lower than ≈150 ppm to reduce the formation of borides [19].

The modern 9-12% Cr steels are alloyed with both boron and nitrogen to achieve precipitation strengthening from fine MX nitrides together with the boro-carbide stabilization. It is thus important to balance the boron and nitrogen concentrations to avoid precipitation of BN particles. This can be done by the solubility product for BN given by:

$$\log[\%B] = -2.45\log[\%N] - 6.81 \quad (5.2)$$

The product is valid for 1050-1150 °C, where %B and %N are the soluble contents of boron and nitrogen in mass.% [20].

**Segregation of boron to GBs**

The segregation of B atoms to GBs has been widely studied in austenitic steels [8, 12, 21], and results from these studies are highly relevant also to the 9-12% Cr martensitic steels, since they have an austenitic microstructure at the normalizing temperature and during cooling after normalization until the martensite transformation begins at 400-200 °C. Two mechanisms for B segregation to austenite GBs have been proposed: equilibrium segregation and non-equilibrium segregation.

Equilibrium segregation to GBs occurs at temperatures which are sufficiently high to allow the diffusion of boron. The driving force is the reduction of free energy by moving boron from the grain interior to the GBs [21]. The amount of equilibrium segregated boron atoms increases with reduced temperature (below ≈700 °C).
Non-equilibrium segregation occurs during cooling from the normalizing temperature. Sufficiently fast cooling generates a surplus of vacancies in steels, which annihilate at GBs and thus generate a vacancy flow to the boundaries. In boron alloyed steels boron-vacancy complexes are formed and transported to austenite GBs, where the vacancies annihilate and leave boron atoms behind [13, 21]. The phenomena of non-equilibrium segregation of B was proposed by Westbrook in 1964 [22] and then Aust [23] and Antony [24] established a model for the non-equilibrium segregation, which states that the mobility of the solute atom-vacancy complexes is higher than the mobility of solute atoms themselves. Hence, the boron back-diffusion is slower than the supply rate of new complexes, and the process maintains a boron flow to boundaries throughout the cooling. The amount of boron segregated by non-equilibrium mechanism is strongly dependent on the cooling rate, and it is largest at some intermediate cooling rate [8, 21, 25, 26, 27, 28, 29, 30]. Boron segregation is strongest at the beginning of cooling when the temperature and, therefore, mobility of atoms is highest [31]. In contrast to the equilibrium segregation, which is localized to within a few atomic layers at the boundaries, the non-equilibrium segregation results in a much wider zone enriched by boron [12, 28, 31, 32].

It is generally accepted, that the amount of B atoms segregated onto austenite GBs in steels is highly dependent on the holding temperature, cooling rate, the character of the GB, the boron concentration in the steel, and the presence of other B-containing phases [28, 33]. In addition it is found that B segregation is influenced by alloying with Mo at a relatively low cooling rate of 5°C/s [33]. There is, however, controversy about the prevailing mechanism for boron segregation to austenite grain boundaries during cooling of low alloyed martensitic steels [8, 25, 26, 31, 33, 34]. Li [34] and Shigesato [29] suggested that B segregates by the non-equilibrium mechanism. However, Takahashi [33] claimed that B segregation occurs by diffusion limited equilibrium segregation in B and Mo-added martensitic steels.

Since the segregation of boron has a strong influence on the distribution of boron in the 9-12% Cr steels after normalizing and tempering, a detailed quantitative description of this process is a key to the control and optimization of boron in the martensitic creep-resistant steels. However, due to experimental difficulties only very limited quantitative infor-
5.3 Boron behaviour in 9-10% Cr martensitic steels

Information on boron in 9-12% Cr martensitic steels is available. Only with the recent advent of electron energy loss spectroscopy (EELS) [29], atom probe, and more recently atom probe tomography (APT) [34, 35, 36, 37] we have begun to get access to experimental data with sufficient accuracy. The aim of the present work is to provide quantitative data by APT for boron behavior in martensitic steels during normalization. We believe that this information is of high importance for the optimization and control of boron in 9-12% Cr martensitic steels.

5.3.2 Experimental

Materials and Heat Treatment

The steels studied in this work are three 9-10% Cr martensitic steels with boron contents varying from 10 to 108 ppm. The first steel is the P92 containing 9% of Cr and 10 ppm of B; the second is a 10% Cr experimental martensitic steel with 72 ppm of B; and the third steel is an industrial steel for large forgings containing 9% of Cr and 108 ppm of B. For simplicity the studied steels are referred to as 10B, 70B and 100B, respectively. Their chemical compositions are given in Table 5.8. The 70B and 100B steels are alloyed with low nitrogen in order to avoid BN precipitates. In addition the 70B steel contains titanium to tie up N by the formation of TiN.

Cubic samples of all investigated steels with a side length of 15 mm were normalized at 1100 °C for 1 h and cooled in air to room temperature to provoke segregation of B atoms onto austenite grain boundaries.

Experimental techniques

Thin-foils were used for the fabrication of tips for atom probe tomography (APT). They were made by electropolishing in a solution of 10% perchloric acid in ethanol at a temperature of 240K and voltage of 21-23V using a Struers “Tenupol-5” device. Site-specific APT tips, where austenite grain boundaries (PAGB) are located within 100 nm from the tip apex, are required, which makes the preparation of APT tips challenging. In order to speed up successful tip sampling, an improved APT site-specific sample preparation method, involving a custom-made sample holder was developed as described in section 5.5. APT tips were
Table 5.8: The chemical compositions of the studied steels.

<table>
<thead>
<tr>
<th>Steel</th>
<th>10B (w.%)</th>
<th>10B (at.%)</th>
<th>70B (at.%)</th>
<th>70B (w.%)</th>
<th>100B (w.%)</th>
<th>100B (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>bal.</td>
<td>bal.</td>
<td>bal.</td>
<td>bal.</td>
<td>bal.</td>
<td>bal.</td>
</tr>
<tr>
<td>Ni</td>
<td>0.16</td>
<td>0.15</td>
<td>0.18</td>
<td>0.17</td>
<td>0.15</td>
<td>0.14</td>
</tr>
<tr>
<td>Cr</td>
<td>8.97</td>
<td>9.65</td>
<td>10.03</td>
<td>10.8</td>
<td>9.32</td>
<td>9.34</td>
</tr>
<tr>
<td>W</td>
<td>1.8</td>
<td>0.5</td>
<td>2.02</td>
<td>0.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mo</td>
<td>0.5</td>
<td>0.3</td>
<td>0.71</td>
<td>0.4</td>
<td>1.49</td>
<td>0.86</td>
</tr>
<tr>
<td>Nb</td>
<td>0.06</td>
<td>0.04</td>
<td>0.053</td>
<td>0.03</td>
<td>0.05</td>
<td>0.03</td>
</tr>
<tr>
<td>Ti</td>
<td>-</td>
<td>-</td>
<td>0.015</td>
<td>0.004</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Si</td>
<td>0.13</td>
<td>0.26</td>
<td>0.07</td>
<td>0.14</td>
<td>0.084</td>
<td>0.17</td>
</tr>
<tr>
<td>Mn</td>
<td>0.42</td>
<td>0.43</td>
<td>0.13</td>
<td>0.13</td>
<td>0.33</td>
<td>0.33</td>
</tr>
<tr>
<td>C</td>
<td>0.1</td>
<td>0.47</td>
<td>0.087</td>
<td>0.407</td>
<td>0.14</td>
<td>0.65</td>
</tr>
<tr>
<td>N</td>
<td>0.045</td>
<td>0.18</td>
<td>0.003</td>
<td>0.016</td>
<td>0.0197</td>
<td>0.078</td>
</tr>
<tr>
<td>Co</td>
<td>-</td>
<td>-</td>
<td>2.8</td>
<td>2.67</td>
<td>1.25</td>
<td>1.18</td>
</tr>
<tr>
<td>V</td>
<td>0.19</td>
<td>0.21</td>
<td>0.2</td>
<td>0.22</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.029</td>
<td>0.025</td>
</tr>
<tr>
<td>Al</td>
<td>0.01</td>
<td>0.02</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>0.001</td>
<td>0.005</td>
<td>0.0072</td>
<td>0.037</td>
<td>0.0108</td>
<td>0.055</td>
</tr>
</tbody>
</table>

prepared by FEI Helios NanoLab 600 using in-situ lift-out method and dual-beam focus ion beam (FIB) milling. PAGBs were identified by ion tunneling scanning electron microscopy. The PAGBs were oriented 90° to the tips axis. A transmission kikuchi diffraction detector (TKD) was applied in order to track the PAGB during the final milling when the PAGB was placed within the first 100 nm from the top of the APT tip. The final tip radius of the specimen was less than 30 nm. TKD was also used to measure the PAGB misorientation. Further APT tips were extracted from the center of relatively large prior austenite grains to detect the boron concentration away from PAGBs. APT analysis was performed using a local electrode atom probe Imago LEAP 3000X HR. The measurements were carried out in laser mode at 65K with a laser energy of 0.3 nJ and a pulse frequency of 200 kHz [38]. The acquired data were analyzed using IVAS 3.4.1 software from CAMECA. Microstructure observations were made using FEI Helios NanoLab 600 and NanoNova SEMs as well as JEOL2010 TEM.

5.3.3 Results

Normalized microstructures

All materials investigated in the present work were martensitic. Figure 5.28 shows a typical microstructure after normalization at 1100 °C for 1 h obtained by light optical microscopy (Fig. 5.28a), EBSD map (b) and TEM micrograph (c). The martensite microstructures of the in-
Figure 5.28: Typical microstructures of as-quenched at 1100 °C for 1 h high-temperature martensitic steels: LOM microstructure of 70B steel containing δ-Fe (a); EBSD map showing differently oriented PAGBs divided by packets and blocks of martensite (b); TEM martensite lath structure (c); TEM carbon replica showing Nb rich precipitate identified by electron diffraction and INCA chemical analysis (d); TEM thin foil showing Fe₃C precipitates (e); Fe₃C precipitate measured by APT (f).
Figure 5.29: APT measurements in the 10B steel: FIB tunneling identification of PAGs (a), TKD map including a PAGB (b), 3D APT reconstruction map (c), distribution of B atoms (d), 1D concentration profiles of C, B, Mo, W, and Nb perpendicularly oriented to the PAGB (e).

Investigated steels consist of PAGs divided into blocks, packets and laths of martensite. A small amount of $\delta$-ferrite (approximately 8%) was observed only in the 70B steel (Fig. 5.28a). Secondary phase precipitates, such as round-shaped Nb-rich carbonitrides undissolved at the normalizing temperature (Fig. 5.28d) and needle-shaped Fe$_3$C cementite formed by autotempering of martensite (Fig. 5.28e and 5.28f) were detected in all investigated steels commonly to other 9-12% Cr steels [39].

Boron segregation onto PAGBs

Boron in the 10B steel

Fig. 5.29 shows the process of measuring the Boron concentration on a PAGB in the 10B steel. The PAGB selected in the 10B steel (Fig. 5.29a) was placed at the tip apex and identified in the finally sharpened tip (Fig. 5.29b). The misorientation of the PAGB measured by TKD was
5.3 Boron behaviour in 9-10% Cr martensitic steels

Figure 5.30: APT from the center of the PAG in the 10B steel: FIB tunneling for identification of PAGs: white bar shows the place selected for the fabrication of the APT tip (a); B distribution map in the center of the PAG (b).

52° (Fig. 5.29b). B atoms along with C, Mo, W and Nb were found by APT to segregate onto PAGB (Fig. 5.29c, d). 1-D concentration profiles along the tip direction are shown in Fig. 5.29e. The tip fractured at the PAGB during dissolution of the needle, but the measurement results indicate that the peak boron concentration has been measured. The B concentration at the PAGB is 0.8 at.%, which is 160 times higher than the nominal value in the steel (0.005 at.%). Near the PAGB (Fig. 5.29d) the boron concentration was 0.0028 at.%, which is more than half of the nominal value of B in the steel. The amounts of C and W segregated onto the PAGB are 4.4 at.% and 2 at.%, respectively (Fig. 5.29e).

In order to estimate the overall amount of boron located in the microstructure an APT specimen was extracted from the center of an austenite grain as shown in Fig. 5.30a. The distance between PAGBs along the tip axis was 40 µm. The boron detected in the center of the PAG was homogeneously distributed in the measured volume (Fig. 5.30b) with a concentration of 0.0015 at.%, which is 30% of the overall boron content in the steel.

Boron in the 70B steel

Figure 5.31 shows the APT specimen fabricated from the 70B steel. The misorientation of the PAGB selected for APT measurement was 41° (Fig. 5.31a, b). The 3D APT reconstruction map, contained both a
Figure 5.31: APT measurements in the 70B steel: FIB tunneling for identification of PAGs (a); TKD including the PAGB (b); 3D APT reconstruction map including the PAGB and a MLB (c).

PAGB and a martensite lath boundary (MLB), Fig. 5.31c.

The amount of B atoms segregated onto the PAGB in the 70B steel is 0.081 at.%, which is similar to that observed in the 10B steel. The B concentration in the vicinity of the PAGB is 0.029 at.% (Fig. 5.32). C, Mo, W, Nb and Co distribution maps and their 1D concentration profiles are presented in Fig. 5.32. C, W and Mo segregate to the PAGB in amounts of 2.3 at.%, 0.8 at.% and 1.0 at.%, respectively. Co and Cr segregations are not detected, which corresponds to experimental results in [33, 34].

In order to obtain a wider boron concentration profile from the PAGB into the grain, the APT measurement in the 70B steel was chosen for further detailed characterization because of its long run up to 800 nm in length. A series of small cylinders with a diameter of 15 nm oriented along the analysis direction were extracted from the reconstruction and the mass spectra for individual cylinders were quantified. The background level was low due to the small analysis volume, and was subtracted by the embedded function of the analysis software as reported in section 5.5. Fig. 5.33 presents the B profile obtained. The boron
5.3 Boron behaviour in 9-10% Cr martensitic steels

Figure 5.32: APT analysis in the 70B steel: the distribution maps of B, C, Mo, W, Nb and Co atoms and their 1D concentration profiles taken across the investigated PAGB.

Figure 5.33: Boron profile made by APT experimental results in the 70B steel exposed to normalization at 1100 °C. Inset shows the enlarged area taken from the vicinity of the PAGB.
concentration in the matrix up to 800 nm from the PAGB show some fluctuation between boron concentration of 0.02 to 0.035 at.%.

The concentrations of B atoms measured in the center of two selected PAGs with local distances between PAGBs along the tip axis of 35 µm and 30 µm were found to contain 0.0097 at.% and 0.0158 at.%, of B, which is 26-43% of the nominal value of B (0.037 at.%) in the steel (Fig. 5.34).

The analyzed martensite lath boundaries (MLBs) in the 70B steel showed that only C atoms were segregated to MLBs. The segregation occurred at temperatures below martensite start temperature (≈400 °C), where only the interstitial elements are mobile. No other elements were found on the MLBs after normalizing HT. Slightly different concentrations of C (0.76 at.%; 1.00 at.% and 1.16 at.%) were found on three investigated MLBs (Fig. 5.35). B atoms were not found segregated to the MLBs after the martensite transformation, which can be explained by their low mobility at low temperatures. Co and Fe are found to be depleted at MLBs (Fig. 5.35).

**Boron in the 100B steel**

The PAGB selected for APT measurement in the 100B steel was perpendicularly oriented and located at 50 nm from the tip apex as shown
5.3 Boron behaviour in 9-10% Cr martensitic steels

Figure 5.35: Distribution maps of C, Co and Fe atoms and their 1D profiles taken across three MLBs indicating segregation of C in the 70B steel after normalization.
Figure 5.36: APT measurements in the 100B steel: FIB tunneling identification of PAGs (a); 3D APT reconstruction map (b).

in Fig. 5.36a. The misorientation of the PAGB measured by TKD was 52°. Figure 5.36b represents boron (blue) and chromium (pink) atom distributions in the reconstructed APT tip of the 100B steel.

A strong conglomeration area with a flat surface along the PAGB and a thickness of 14 nm, rich in B, Cr, C and Mo was observed in the 100B steel (Fig. 5.37). 1-D concentration profiles taken across the conglomeration area show B and Cr concentrations of 33 at.% and 36 at.% respectively in the conglomeration (Fig. 5.37). In addition Fe and Mo with amounts of 20 at.% and 6 at.% respectively were also present. The composition of the conglomerate indicates an M₂B-type precipitate, where M is Cr; Fe and Mo (Fig. 5.37). This type of borides precipitated on the PAGBs in the 100B steel was also observed in larger scale using SEM (Fig. 5.38). The fine (Cr,Fe)₂B borides formed on a part of the PAGBs during normalization of the 100B steel as reported in detail in section 5.4. It is worth to note, that no such fine borides were detected in the 10B or the 70B steels.

The boron concentration observed in the vicinity of the PAGB is 0.103 at.%, which is almost twice of the overall B content in the steel. However, an oxidized area was observed near the analyzed volume, which resulted in local fluctuations of the boron concentration (Fig. 5.37). APT analysis of the distribution of B in the center of a PAG in the 100B steel is shown in Fig. 5.39a. The boron concentration in the tip with a local distance of
5.3 Boron behaviour in 9-10% Cr martensitic steels

Figure 5.37: Distribution of B, Fe, Co, Cr, C, and Mo atoms and their 1D concentration profiles taken across the PAGB indicating \((\text{Cr,Fe})_2\text{B}\) precipitate formed on the PAGB in the 100B steel.

85 \(\mu\)m between PAGBs along its axis is 0.0147 at.% (Fig. 5.38b), which is 27\% of the nominal boron content in the steel.

5.3.4 Discussions

Boron distribution

Table 5.9 summaries the APT quantitative data obtained for B atoms in different parts of the PAGs: in the matrix of investigated martensite steels, at the PAGBs and in the vicinity of PAGBs in comparison with the nominal concentrations of B. The boron concentrations on the PAGBs in the 10B and the 70B steels are similar at 0.8 at.\%, irrespective of the boron content in the steel.

Miyamoto found by APT for a low alloy 0.19C-1.99Mn steel with 11 ppm B that the B segregation at PAGBs after water quenching from 1200 °C is increased with increasing boundary misorientation angle of up to 30°. After that the amount of segregated boron became constant at approximately 2 at.\%, [41]. Concentration profiles measured by APT in the low alloy steel were of similar width as in the present 10B and
Figure 5.38: SEM electron backscatter image of the fine PAGB borides detected in the 100B steel after normalization at 1100 °C.
5.3 Boron behaviour in 9-10% Cr martensitic steels

70B steels. The investigated PAGBs in the 10B and 70B steels have misorientation angles of 52° and 41°, respectively, which could indicate that the grain boundary boron concentration has reached a saturation level. The lower grain boundary concentration in the present steel compared to the low alloy steel could be due to the high Cr content and to the slower cooling rate.

In the center of the PAGBs we measured concentrations between 25 and 35% of the nominal boron concentrations in all steels. This is not in agreement with results reported in [34], where boron was absent in the martensite matrix of a low alloy 0.19C-1.2Mn-0.2Cr-0.5Mo steel with 12 ppm B after normalizing at 930 °C followed by water quenching; moreover, in the mentioned work the small amount of B atoms observed in the matrix was attributed to background noise signal. Similar to the results by [41] the PAGB concentrations of boron were close to 2% and profiles were of similar width as in the present investigations. Again this indicates that either the slower cooling or the high Cr content leads to less boron segregation.

Boron found by APT

The average grain sizes of the 10B and 70B steels were measured by linear intercept to 25 μm and 50 μm, respectively. Taking a grain boundary width of 10 nm the grain boundary volume fractions in the two steels are

Figure 5.39: APT taken from the center of the PAG in the 100B steel: FIB tunneling identification of PAGs: white bar shows the place selected for the APT specimen (a); B distribution map in the center of the PAG (b).
Table 5.9: Boron distributions in the studied 9-10% Cr martensitic steels, obtained by APT after normalization at 1100 °C for 1 h.

<table>
<thead>
<tr>
<th>Steel</th>
<th>Concentration of B, atomic, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>nominal</td>
</tr>
<tr>
<td>10B steel</td>
<td>50</td>
</tr>
<tr>
<td>70B steel</td>
<td>370</td>
</tr>
<tr>
<td>100B steel</td>
<td>550</td>
</tr>
</tbody>
</table>

0.12% and 0.06%, respectively. Assuming similar boron concentrations of 0.8 at.% on all boundaries 20% of the added boron in the 10B steel and 1.3% of the added boron in the 70B is located on the PAGBs after segregation. Assuming the near grain boundary region to have a width of 1 µm in both steels (figure 5.33), and using the boron concentrations measured near the PAGBs of 0.0028 at.% in the 10B steel and 0.03 at.% in the 70B steel indicates that 12% of the added boron in the 10B steel and 9% of the added boron in the 70B steel is located in the near PAGB regions. The grain interiors account for 80% of the grain volume containing 24% of the added boron of the 10B steel and for 88% of the grain volume containing 23-38% of the added boron to the 70B steel. This means that the APT measurements account for totally 46% of the boron added to the 10B steel and 33-56% of the boron added to the 70B steel. Thus, a significant amount of the boron in both steels should be located in precipitates.

Boron-containing precipitates

SEM microstructure observations revealed coarse precipitates in the matrix of the 10B steel. These precipitates with round shape and an average size of 5 µm were enriched in B and N as shown by EDS (Fig. 5.40). They are assumed to be BN boronitrides. Their volume fraction was low, since only few precipitates of this type were detected on an area of approximately 300 x 300 µm.

In the 100B steel BN boronitrides were found quickly in the SEM since they formed particle clusters, as shown in Fig. 5.41. The average size of such clusters was estimated at about 20 µm and the volume fraction of the BN precipitates was higher than that in the 10B steel. The microstructure observations in the 70B steel did not reveal BN
5.3 Boron behaviour in 9-10% Cr martensitic steels

Figure 5.40: BN nitrides found after normalization at 1100 °C of the 70B steel; SEM electron backscatter image (a); EDS maps of B, N, Cr and Fe (b).

Figure 5.41: BN nitrides found after normalization at 1100 °C of the 100B steel; SEM electron backscatter image (a); EDS maps of B, N, Cr and Fe (b).
Figure 5.42: SEM electron backscatter image of TiN nitrides with different shape found after normalization at 1100 °C of the 70B steel.

Table 5.10: Calculated and measured boron concentrations in the steel matrix of measured steels.

<table>
<thead>
<tr>
<th>Steel</th>
<th>In steel</th>
<th>M₂B</th>
<th>BN</th>
<th>APT</th>
</tr>
</thead>
<tbody>
<tr>
<td>100B</td>
<td>550</td>
<td>75</td>
<td>140</td>
<td>147</td>
</tr>
<tr>
<td>70B</td>
<td>370</td>
<td>90</td>
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<td>97/158</td>
</tr>
<tr>
<td>10B</td>
<td>50</td>
<td>50</td>
<td>34</td>
<td>15</td>
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</tbody>
</table>

The calculations indicate that M₂B boride should be stable in the 100B steel at normalizing temperature. However, the calculated boron concentration in the austenite FCC matrix at 1100 °C is only half of the measured value. Also heat treatment experiments in [40] show that the observed fine M₂B particles were dissolved at 1100 °C.
5.3 Boron behaviour in 9-10% Cr martensitic steels

The SEM investigations revealed large conglomerates of BN most probably formed during cooling after solidification forging [20]. Equilibrium calculations performed with borides suppressed and with only BN allowed to form, show that the boron concentration in the FCC matrix reaches a value close to the one measured by APT at approximately 900 °C, table 5.10.

Calculations for the 10B steel show that all boron should be in solid solution at 1100 °C, which indicate that the observed BN particles form during cooling from 1100 °C. Calculations at 850 °C indicate that borides of type M₂B or M₃B₂ should be stable. However if the borides are suppressed from the calculations (simulating that they cannot nucleate) BN appears as an equilibrium phase leaving a little more than half of the boron in solid solution in the FCC matrix.

Thus coarse BN particles in the 10B steel seem to explain the missing boron content not accounted for by the APT measurements.

Calculations for the 70B steel indicate that M₂B borides with a volume fraction of 0.083% should be stable at 1100 °C leaving only 25% of the added boron in solution. However, the APT measurements indicated that 30-50% of the added boron was in solution. Due to the Ti addition no BN can form in this steel, and the SEM investigations did not reveal any boron rich precipitates. Thus, for the 70B steel we have not revealed the location of the missing boron.

Segregation mechanisms

Initial modeling of concentration profiles developed during cooling was made with finite difference simulations. When assuming non-equilibrium segregation as described by Karlsson et.al. [28] the model resulted in far too low grain boundary concentrations. When assuming diffusion limited equilibrium segregation a wide boron depleted zone develops near the grain boundaries. Thus, at present none of the simulations provide a good description of the measured concentration profiles and it is not possible to determine the GB segregation mechanism.

5.3.5 Conclusions

The boron behaviour in three 9-11% Cr martensitic steels containing 10, 72 and 108 at.% of B (10B, 70B and 100B, respectively) was investigated
after normalization at 1100°C. The following conclusions were stated:

- B segregated to austenite grain boundaries during air cooling from normalization at 1100 °C in similar amount of 0.8 at.% in the 10B and 70B steels.

- After segregation to austenite GBs significant amount of boron remained in the matrix of all investigated steels.

- Fine Cr-rich M$_2$B borides with average thickness of 15 nm were observed on PAGBs only in the 100B steel, while in the 10B and 70B steels PAGBs remained boride-free.

- Only C atoms segregated onto MLBs during normalization, while PAGBs were enriched by C, V, Mo, Nb, W and B.

- BN nitrides were found in the 10B and the 100B steels, while the 70B steel was found to be BN-free because of addition of Ti which forms TiN nitrides.

- Measured concentration profile does not correlate with theoretical profiles according to diffusion limited segregation mechanism or non-equilibrium segregation mechanism.

Acknowledgments

This work was financially supported by Siemens AG. FL is partly funded via the Swedish Energy Agency and LIGHTer, a program financed within Strategic Innovation Areas, a mutual venture between VINNOVA, the Swedish Energy Agency, and Formas.

Bibliography


5.4 Fine (Cr,Fe)\(_2\)B borides on grain boundaries in a 10Cr-0.01B martensitic steel

5.4 Fine (Cr,Fe)\(_2\)B borides on grain boundaries in a 10Cr-0.01B martensitic steel


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Abstract

A 10Cr creep resistant martensitic steel with 108 ppm B was normalized at 1100 °C for 1 h and air cooled. Fine (Cr,Fe)\(_2\)B borides were observed on the majority of prior austenite grain boundaries, all of which were high angle boundaries, as revealed by EBSD-based reconstruction of parent austenite grains. Some high angle boundaries including twin boundaries were boride-free. Segregation of boron to austenite grain boundaries during slow cooling from 1100 °C led to boride nucleation and growth. Their size increased with decreasing cooling rate. Borides were verified by atom probe tomography, auger spectroscopy, transmission and scanning electron microscopy.

*Keywords: martensitic steels; borides; atom probe tomography; boron behavior.*

9-12% Cr martensitic creep resistant steels are applied in pressurised steam power plant components, such as pipes, turbine casings and rotors, operating at elevated temperatures up to 620 °C. High stability of the tempered martensite microstructure under service loads is achieved by precipitation of M\(_{23}\)C\(_6\) carbides, MX nitrides and intermetallic Laves phase. The presence of fine precipitates is facilitated by normalizing
and tempering quality heat treatment. Normalizing consists of heating between 1020 °C and 1150 °C, whereby austenite is formed and precipitate phases are largely dissolved. During subsequent cooling, martensite transformation begins at 400 °C to 200 °C (mainly depending on the carbon content), and is almost complete at room temperature. The hard and brittle martensite is then softened during tempering at 620-780 °C when $M_{23}C_6$ carbides and MX nitrides precipitate [1, 2]. The addition of a small amount (about 20-150 ppm) of B has been found to significantly improve creep strength of the martensitic 9-12%Cr steels [3]. The influence of boron on creep strength is attributed to the incorporation of boron into $M_{23}(C,B)_6$ carbides during tempering, whereby their coarsening rate during creep is reduced [4, 5, 6, 7]. However, details of boron behaviour in martensitic creep resistant steels are not well-understood.

For austenitic steels, it is well documented that boron segregates to austenite grain boundaries (GBs) during cooling after solution treatment, and that segregated boron atoms can lead to formation of boron-rich precipitates on austenite GBs [8–12]. Similar boron segregation has also been found in 9-12% Cr steels and other martensitic steels [6, 13, 14, 15], which is to be expected, since martensitic steels are austenitic during cooling from the normalizing temperature until the martensite transformation begins. Studies of boron in 9-12% Cr steels have mainly focused on the as-tempered or creep exposed conditions [4, 16, 17, 18, 19]. In such martensitic steels, borides have been found as large particles presumably formed from the melt during solidification, and particularly, the formation of BN particles has been described in detail [4, 16, 18, 19, 20, 21]. In the present work, we focus on studying boron behaviour at GBs in a 10% Cr steel during the normalization using a variety of advanced experimental techniques for specimen preparation and characterization.

The investigated material was taken from a large forging of a martensitic steel (9.32% Cr, 1.49% Mo, 0.05% Nb, 0.33% Mn, 0.14% C, 0.002% N, 1.25% Co, 0.2% V, and 0.0108% B, wt.% bal. Fe) after normalization and tempering quality heat treatment. A cubic sample with a side length of 15 mm was heated to 1100 °C for 1 h followed by air cooling to provoke boron segregation. Atom probe tomography (APT) was chosen for quantification of boron content at prior austenite grain boundaries (PAGBs) in a specimen prepared using in-situ lift-out method in a fo-
cused ion beam and scanning electron microscope (FIB/SEM) FEI Helios NanoLab 600. The final radius of this specimen tip was less than 50 nm. The PAGB in the APT specimen was identified by ion tunneling contrast of FIB microscopy. The PAGB was oriented 90° to the tip axis to simplify its recognition at the final tip sharpening process and also to ensure the presence of this PAGB in the final tip. Transmission Kikuchi diffraction with a step size of 10 nm was used to track the PAGB during final milling, and its misorientation angle was measured to be $\theta = 52^\circ$.

The APT analysis was performed using a local electrode atom probe Imago LEAP 3000X HR in the laser mode at -218° with laser energy of 0.3 nJ and a pulse frequency of 200 kHz. The acquired data were analysed using IVAS 3.4.1 software from CAMECA. The reconstructed APT tip contained approximately $26 \times 10^6$ atoms.

The APT results reveal a conglomeration enriched by B, Cr, Fe, Mo, V, Nb and C in the vicinity of the PAGB. The distribution of B atoms is presented in Fig. 5.43. The conglomeration has a semi-ellipsoid shape with a flat surface along the PAGB and a maximum thickness of 14 nm in the APT analyzed volume. The conglomeration was isolated by an isoconcentration surface (at a B concentration of 29 at.%) containing $226 \times 10^3$ atoms with composition: 33% B, 36% Cr, 21% Fe, 6% Mo, 2% V, 0.07% Nb and 2% C (all in at.%) (Table 5.11). The quantification was performed according to [22]. This composition corresponds to a M$_2$B-type precipitate, where M is mainly Cr, Fe, and Mo atoms. 1D concentration profiles were calculated along a cylinder volume with a diameter of 10 nm perpendicular to the flat surface corresponding to the PAGB (Fig. 5.43 b).

Taking into account that fine Cr-rich borides of this type have not been previously observed in as-normalised martensitic 9-12%Cr steels, our APT results indicating the presence of the M$_2$B-type precipitate are surprising. In contrast to the martensitic steels, Cr-rich M$_2$X borides were found by atom probe in two 17Cr-13Ni austenitic steels containing 23 and 40 ppm of B [23] (see Table 5.11). The borides observed in both the austenitic steels and our martensitic steel contained significant amounts of carbon. Additionally, the boride in the present work is enriched by V and Nb.

To verify our findings on a larger scale, scanning electron microscopy (SEM), Auger spectroscopy on thin foil and transmission electron mi-
Figure 5.43: APT analysis of a boride in the vicinity of PAGB with a misorientation angle of 52°: (a) distribution of boron atoms; (b) a linear concentration profile through the boride (all in at.%).
5.4 Fine (Cr,Fe)$_2$B borides on grain boundaries in a 10Cr-0.01B martensitic steel

Table 5.11: The chemical composition of borides analyzed by APT in present work in the 10Cr-0.01B martensitic steels and in austenitic steels studied in [23] (all in at.%).

<table>
<thead>
<tr>
<th>Borides</th>
<th>B</th>
<th>Cr</th>
<th>Fe</th>
<th>Mo</th>
<th>C</th>
<th>V</th>
<th>Co</th>
<th>Nb</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_{1.8}$(B,C)</td>
<td>33.0</td>
<td>36.1</td>
<td>20.9</td>
<td>5.2</td>
<td>2.1</td>
<td>2.3</td>
<td>0.2</td>
<td>0.07</td>
<td>0.2</td>
</tr>
<tr>
<td>$M_{1.7}$(B,C)</td>
<td>35.0</td>
<td>29.5</td>
<td>12.9</td>
<td>20.5</td>
<td>1.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.6</td>
</tr>
<tr>
<td>$M_{2.7}$(B,C)</td>
<td>25.2</td>
<td>36.0</td>
<td>9.8</td>
<td>26.8</td>
<td>2.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Microscopy (TEM) on extraction replicas were applied. All techniques revealed chains of fine precipitates at PAGBs with sizes similar to the one found by APT. For Auger spectroscopy, a thin foil was prepared by jet-electropolishing in 10% perchloric acid in ethanol at -33 °C and 22 V using Struers “Tenupol-5”, and the measurements were made in a PHI 700 Scanning Auger electron spectroscope. A gentle argon ion sputtering was used to remove the surface contamination prior to data acquisition. The accelerating voltage was 10 kV and the beam current was 10 nA.

Typical Auger spectra taken from a PAGB precipitate and matrix are presented in Fig. 5.44, where boron is identified in the precipitate (encircled in Fig. 5.44 a). More GB precipitates were investigated by energy dispersive x-ray spectroscopy (EDS) on carbon extraction replicas made by a Q150R E carbon coater and detached from the bulk by electrolytic etching in a solution of 5% hydrochloric acid in ethanol. The replicas were investigated using a JEOL 3000F field emission gun (FEG) TEM, where PAGBs were identified by the traces of triple junctions (Fig. 5.45 a).

Fine precipitates were observed only on the PAGBs, but not on martensite block, packet or lath boundaries or anywhere else within the martensite matrix. The EDS system used in the present work did not allow quantitative analysis of boron. Therefore, the average chemical composition was corrected assuming the presence of 33.3 at.% boron. The corrected average chemical composition for at least 8 randomly chosen PAGB precipitates is consistent with the APT results (Fig. 5.45, Table 5.12). The mean size of the observed borides is approximately 15 nm in width and 95 nm in length along the PGB, i.e. they have similar thickness as the conglomeration observed in APT, and their length is 6 times their thickness, which is similar to borides observed by Karlsson.
and Nordén [23] and Sourmail et. al. [24].

According to [23], the presence and the size of borides in austenitic steels were highly dependent on the cooling rate after solution treatment. In the steels investigated in [23], borides were not observed after water quenching, but were found after air and furnace cooling, and their average size increased from 50 to 700 nm with decreasing cooling rate.

To investigate whether there is a similar tendency in the present martensitic creep resistant steel, normalization at 1100 °C for 1 h was followed by fast cooling in water (within 5 s) or slow cooling in furnace (within 8 h) to room temperature. SEM observations showed behavior similar to that in the austenitic steels: no PAGBs with borides were found in the specimen heat treated with fast cooling rate. This indicates that the borides are dissolved at 1100 °C; and that they nucleate and grow during cooling from the normalization temperature. Furthermore, it was found that slow cooling led to increased growth of PAGB borides as compared to air cooling. The mean size of the borides grown during slow cooling in furnace could not be measured on the carbon replicas because they did not extract large precipitates with the technique used. Based on SEM observations, their maximum length was established to be approximately 300 nm.

Thus, the evolution of borides in the austenitic steels [23] and in the present martensitic steel is qualitatively similar. The chemical composition of the borides was found to change significantly with cooling rate (see Table 5.12).

It is known that M$_2$B type borides can have tetragonal (space group 14/mcm) or orthorhombic (space group Fddd) crystal structures [12, 23, 25]. For example, Karlsson and Nordén [23] found a Mo-free M$_2$B phase with the orthorhombic structure and Mo containing M$_2$B with the tetragonal structure. Although attempts were made to identify the crystal structure of the PAGB borides by electron diffraction in our work, the diffraction patterns obtained did not match any of the suggested crystal structures. This could be due to a mixture of orthorhombic and tetragonal structures as observed in [23]. Further investigations are required to analyze the crystallography of M$_2$B borides and the orientation relationships between M$_2$B precipitates and the martensite matrix.

Phase equilibrium calculations made for the present steel composition using Thermo-Calc version 2017b with the TCFE9 database [26]
5.4 Fine (Cr,Fe)$_2$B borides on grain boundaries in a 10Cr-0.01B martensitic steel

**Figure 5.44:** Auger spectroscopy data from the martensitic steel containing 108 ppm of B in the as-normalized condition: (a) a region containing a PAGB, where boron-rich precipitates are seen as bright features; (b) spectra taken from the encircled areas representing a PAGB precipitate (red circle) and the martensitic matrix (black circle).
Figure 5.45: TEM micrographs from a carbon replica in the 10Cr-0.01B martensitic steel: (a) triple junction of PAGB traces; (b) a high magnification image showing M$_2$B borides in the area framed in (a) along with their chemical compositions (without B) as measured by EDS (all in at.%).
5.4 Fine $(\text{Cr,Fe})_2\text{B}$ borides on grain boundaries in a 10Cr-0.01B martensitic steel

Table 5.12: Chemical compositions of $M_2\text{B}$ borides formed in the 10Cr-0.01B martensitic steel cooled either in water, air or furnace and measured by EDS on extraction replicas or by APT. The measurement results are compared with calculations by Thermocalc (all in at.%). $^a$Average values calculated on 8 randomly chosen precipitates.

<table>
<thead>
<tr>
<th>Cooling media</th>
<th>Fe</th>
<th>Cr</th>
<th>B</th>
<th>Mo</th>
<th>Mn</th>
<th>V</th>
<th>Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water (EDS)$^a$</td>
<td>30.6 ± 1.8</td>
<td>56.2 ± 2.1</td>
<td>-</td>
<td>9.6 ± 0.9</td>
<td>0</td>
<td>2.6 ± 0.3</td>
<td>1.0 ± 0.1</td>
</tr>
<tr>
<td>Air (EDS)$^a$</td>
<td>23.2 ± 1.2</td>
<td>58.2 ± 2.5</td>
<td>-</td>
<td>7.6 ± 0.6</td>
<td>0</td>
<td>7.4 ± 0.4</td>
<td>3.6 ± 0.3</td>
</tr>
<tr>
<td>Air (APT)</td>
<td>20.9</td>
<td>36.1</td>
<td>33</td>
<td>5.2</td>
<td>0.2</td>
<td>2.3</td>
<td>0.07</td>
</tr>
<tr>
<td>Air (EDS) including boron</td>
<td>20.4</td>
<td>37.5</td>
<td>33.3</td>
<td>6.4</td>
<td>0</td>
<td>1.7</td>
<td>0.7</td>
</tr>
<tr>
<td>Furnace (EDS) including boron</td>
<td>15.5</td>
<td>38.8</td>
<td>33.3</td>
<td>5.1</td>
<td>0</td>
<td>4.9</td>
<td>2.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Fe</th>
<th>Cr</th>
<th>B</th>
<th>Mo</th>
<th>Mn</th>
<th>V</th>
<th>Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>1100 °C</td>
<td>31.2</td>
<td>32.4</td>
<td>33.3</td>
<td>2.6</td>
<td>0.33</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>700 °C</td>
<td>20.5</td>
<td>35.4</td>
<td>33.3</td>
<td>10.5</td>
<td>0.29</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>606 °C</td>
<td>15.5</td>
<td>32.6</td>
<td>33.3</td>
<td>18.4</td>
<td>0.24</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Predict that orthorhombic $M_2\text{B}$ is stable in the temperature range from 1200 °C to 1160 °C. Below 1160 °C a molybdenum-rich $M_3\text{B}_2$ with D5A crystal structure is predicted to be the most stable boride. However, when $M_3\text{B}_2$ is suspended from the equilibrium calculations, thus simulating a situation where $M_3\text{B}_2$ cannot nucleate, orthorhombic $M_2\text{B}$ is predicted to be stable. When the orthorhombic $M_2\text{B}$ is then suspended, the tetragonal $M_2\text{B}$ structure becomes stable. Comparing measured and calculated compositions, the calculated $M_3\text{B}_2$ and tetragonal $M_2\text{B}$ compositions are found to contain far too much Mo. The existing thermodynamic model for orthorhombic $M_2\text{B}$ gives a better agreement, though it has no description for V, Nb and C contents in the phase (Table 5.12).

In the present steel, SEM investigations revealed borides on most of the PAGBs both for air cooling and furnace cooling, where the average size of austenite grains was approximately 100 µm. The number of boundaries with borides in our work is much higher than in a 25Cr-22Ni austenitic steel containing 27 ppm B after solution treatment 1160 °C and cooling at 10 °C/s to 1060 °C followed by water quenching [24], where Cr$_2$B particles were observed only on a few austenite GBs. In [23] the density of fine boride precipitates was found to be similar at all grain boundaries for the 40 ppm B austenitic steel cooled at 13 °C/s
Figure 5.46: One region investigated using both BSE and EBSD: (a) EBSD map, where high angle boundaries are shown as black lines; (b) a high magnification BSE image of the area framed in (a), which contains one boride-free PAGB and two PAGBs with borides seen as bright features; (c) Parent austenite grains reconstructed using the ARPGE software. Boundaries identified as Σ3 twin boundaries are shown as red lines. Deviations from the straight twin boundary morphology are reconstruction artifacts. Angles of misorientations between the reconstructed austenite grains 1 to 8 are shown on the right-hand side.
from 1250 °C and for the 23 ppm boron steel cooled at 31 °C/s from 1250 °C. To investigate any sensitivity of boride precipitation to the GB misorientation in the present martensitic steel, electron backscatter diffraction (EBSD) with a step size of 150 nm was performed in a Zeiss 35 Supra FEGSEM. The investigated region contained several prior austenite grains (PAGs), with martensite blocks, packets and laths (Fig. 5.46 a). In this region, precipitates were found on a number of PAGBs (exemplified in Fig. 5.46 b). Parent austenite grains were then reconstructed from the EBSD data using the ARPGE software [27] and applying Nishiyama–Wasserman orientation relationships. The result of this reconstruction is presented in Fig. 5.46 c, where it is seen that reconstructed austenite GBs are boundaries with misorientation angles between 21° and 60°. Analysis of the reconstructed austenite GBs did not reveal correlations between their misorientations and the presence of fine borides, except for twin boundaries which were all boride-free. The absence of borides on some PAGBs can be attributed to suppressed nucleation, where GB plane orientation is the main controlling factor as suggested in [24]. As follows from the observation of the flat interface in Fig. 5.43 a, the borides need GB planes, where they can form coherent or semi-coherent interfaces, in order to ease nucleation.

The observed formation of fine (Cr,Fe)\(_2\)B borides on GBs during normalization will influence the subsequent nucleation and growth of M\(_{23}\)(C,B)\(_6\) carbides on PAGBs during tempering and creep. The borides could enhance nucleation of carbides by acting as nucleation sites, and they can delay the carbide growth, both by blocking grain boundary diffusion and by hard impingement with the carbides. Abe [28] observed retarded growth of M\(_{23}\)(C,B)\(_6\) carbides on PAGBs during ageing for more than 10,000 hours at 650 °C in 9%Cr steels with boron contents of 100 ppm and more. The resulting retarded carbide growth can in turn significantly affect the mechanical properties of martensitic steels, in particular, their creep resistance.

In summary, advanced techniques, such as APT, FIB and Auger spectroscopy were applied to locally detect small concentrations of boron at PAGBs in a 10Cr martensitic creep resistant steel containing 108 ppm of B. A M\(_2\)B boride with composition: 33% B, 36% Cr, 21% Fe, 6% Mo, 2% V, 0.07% Nb and 2% C (all in at.%) was found by APT at a PAGB after normalizing at 1100 °C and cooling in air. Borides with similar
sizes and compositions were found by Auger spectroscopy, SEM and TEM. The majority of the PAGBs identified using SEM were decorated by fine borides with an average size of \(95 \times 15\) nm. Reconstruction of parent austenite grains based on the EBSD data revealed boride-rich and boride-free high angle GBs. Twin boundaries within reconstructed austenite grains were boride-free. A strong influence of the cooling rate was found on boride formation: water cooling suppressed boride formation, while slower cooling led to enhanced growth of the borides. It is concluded that the fine PAGB \(M_2B\) borides were absent at 1100 °C and that they nucleate and grow after boron segregates to austenite GBs during cooling from the normalization temperature. A reasonable agreement was obtained between measured compositions of the borides and compositions obtained by phase equilibrium calculations.

**Acknowledgments**

This work was financially supported by Siemens AG. FL is partly funded via the Swedish Energy Agency and LIGHTer, a program financed within Strategic Innovation Areas, a mutual venture between VINNOVA, the Swedish Energy Agency, and Formas. The authors thank Dr. C. Cayron for providing the ARPGE software. We are grateful to Prof. Hans-Olof Andrén for valuable discussions.

**Bibliography**


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5.5 Analysing boron in 9–12% chromium steels using atom probe tomography

This section describes the technique used for analysing of boron by atom probe tomography. This work was made in collaboration with our colleagues from APT group at Chalmers. Though, most of results for the manuscript were provided by them, it was worth to include the joint paper in the present Ph.D thesis as the relevant techniques are described.

(submitted to Microscopy and Microanalysis)

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Abstract

Small additions of boron can remarkably improve the long-term creep resistance of 9–12% Cr steels. The improvement has been attributed to boron segregation to grain boundaries during quenching, and subsequent boron incorporation into certain families of precipitates during tempering. However, the detailed mechanisms are not yet fully understood. Atom probe tomography (APT) is an excellent instrument to gain insights in the boron distribution, however, in order to acquire accurate analysis of boron in 9–12% Cr steels using APT, there are several key challenges. In order to better understand and address these challenges, we developed a novel method for site-specific APT specimen preparation, which enables convenient preparation of specimens containing specifically selected grain boundaries positioned approximately perpendicular to the axis of the APT tip. Additionally, when analysing boron at boundaries and in carbides (as diluted solute) and borides, it was repeatedly observed widening of the profile of boron distribution
compared to other elements. This phenomenon is particularly analysed and discussed in light of the evaporation field of the different elements. Finally, the possible effects of detector dead-time on quantitative analysis of boron in metal borides are discussed. A simple method using 10B correction was used to obtain good quantification.

Key words: custom-made specimen holder, TKD, prior austenite grain boundaries, equilibrium segregation, non-equilibrium segregation, precipitates, carbides, borides, quantification.

Introduction

Boron has long been found beneficial to steels. For instance, small additions (usually several tens of ppm) of boron can remarkably improve the hardenability of low alloy steels \[1, 2\], and increase the long-term creep resistance of 9–12% Cr steels \[3\]. The latter type of steels are widely used for thick section components in steam power plants that generate more than 60% of the electricity worldwide. The improvement in creep resistance was attributed to boron segregation to grain boundaries during quenching, and subsequent boron incorporation into certain families of precipitates during tempering \[4, 5\]. However, the detailed mechanisms are not yet fully understood, mainly due to the following three reasons. Firstly, boron is the fifth lightest element. Secondly, the boron concentration can be rather low, for instance, for grain boundary segregation, the concentration can be well below 1 at.%. Thirdly, boron atoms are often distributed in very small regions, such as boundaries and nano-sized precipitates. The combination of all these factors excludes many analytical techniques, for instance, X-ray energy dispersive spectroscopy (not sensitive to light elements); secondary ion mass spectrometry and X-ray photoelectron spectroscopy (not enough spatial resolution); Auger electron spectroscopy (not sufficiently low detection limit). Electron energy loss spectroscopy attached to a transmission electron microscopy can potentially be used \[6, 7\], however handling magnetic specimens like 9–12% Cr steels and at the same time looking for low concentration of B from small areas is far from trivial. Thus atom probe tomography (APT) makes an ideal instrument for analysing B in 9–12% Cr ferritic/martensitic steels, because of its equally high sensitivity to all elements, and high spatial resolution – potentially close
Analysing boron in 9–12% chromium steels using atom probe tomography

However, in order to acquire accurate analysis of boron in 9–12% Cr steels using APT, there are several key challenges. As mentioned above, boron atoms are often enriched in small and highly site-specific regions, like grain boundaries, which makes specimen preparation for APT demanding. Additionally, boron, together with C, is known to have a relatively high evaporation field compared to many other elements, such as iron and chromium, which makes it complex to interpret local B distribution in relation to other elements. The calculated evaporation fields for the pure elements are 64 V nm$^{-1}$ for B, 103 V nm$^{-1}$ for C, 33 V nm$^{-1}$ for Fe and 27 V nm$^{-1}$ for Cr; B and C in a steel matrix or in precipitates are also expected to have a higher evaporation field than Fe or Cr in the matrix. Furthermore, boron atoms also have the tendency to evaporate together and form multi-hits, which makes accurate quantification difficult. In this study, we present a novel method for site-specific APT specimen preparation using a custom-made specimen holder for in-situ Focused Ion Beam/Scanning Electron Microscopy (FIB/SEM) lift-out, combined with imaging using ion channeling contrast and Transmission Kikuchi Diffraction (TKD), which enables reliable preparation of APT specimens containing specifically selected grain boundaries. Additionally, the possible widening of boron distribution profiles over boundaries and interfaces (between carbides or borides and the steel matrix) compared to other elements is particularly analysed and discussed in light of the evaporation field of the different elements. Finally, by comparing the multiple and single hits of metal borides, we also discuss the possible effects of detector dead-time on quantitative analysis of boron in metal borides. We propose a simple correction method by using the 10B peaks to obtain a more accurate B concentration.

5.5.1 Materials and methods

Materials

Several 9–12% Cr steels were analysed, including three experimental alloys (TAF B, FT3B, and Z_Nb) and one commercial 10% Cr alloy (Mat-B). Their chemical compositions are listed in Table 5.13 and heat treatment conditions are listed in Table 5.14. The general microstructure
of the steels was studied with a LEO Ultra 55 (Zeiss AG, Oberkochen, Germany) Scanning Electron Microscope (SEM) equipped with a field emission gun. The accelerating voltage was 20 kV. The specimens were etched with Villela’s reagent, consisting of 45 ml glycerol, 45 ml nitric acid, and 30 ml hydrochloric acid. The preferential chemical etching of the steel matrix compared to the precipitates, which are preferentially located at PAGBs and lath boundaries, makes PAGBs and lath boundaries visible.

Table 5.13: Chemical compositions of the steels (in wt.% and Fe in balance).

<table>
<thead>
<tr>
<th>Steel</th>
<th>Z-Nb</th>
<th>TAF B</th>
<th>FT3B</th>
<th>MAT-B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>bal.</td>
<td>bal.</td>
<td>bal.</td>
<td>bal.</td>
</tr>
<tr>
<td>Ni</td>
<td>0.47</td>
<td>&lt;0.002</td>
<td>0.11</td>
<td>-</td>
</tr>
<tr>
<td>Cr</td>
<td>11.64</td>
<td>10.45</td>
<td>9.85</td>
<td>9.30</td>
</tr>
<tr>
<td>W</td>
<td>2.82</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mo</td>
<td>-</td>
<td>1.54</td>
<td>1.48</td>
<td>1.50</td>
</tr>
<tr>
<td>Nb</td>
<td>0.26</td>
<td>0.18</td>
<td>0.07</td>
<td>0.05</td>
</tr>
<tr>
<td>Si</td>
<td>0.30</td>
<td>0.33</td>
<td>0.27</td>
<td>0.08</td>
</tr>
<tr>
<td>Mn</td>
<td>0.50</td>
<td>0.87</td>
<td>1.00</td>
<td>0.30</td>
</tr>
<tr>
<td>C</td>
<td>0.005</td>
<td>0.21</td>
<td>0.20</td>
<td>0.14</td>
</tr>
<tr>
<td>N</td>
<td>0.036</td>
<td>0.017</td>
<td>0.022</td>
<td>0.02</td>
</tr>
<tr>
<td>Co</td>
<td>5.4</td>
<td>-</td>
<td>-</td>
<td>1.25</td>
</tr>
<tr>
<td>V</td>
<td>-</td>
<td>0.24</td>
<td>0.26</td>
<td>0.20</td>
</tr>
<tr>
<td>B</td>
<td>0.004</td>
<td>0.030</td>
<td>0.025</td>
<td>0.010</td>
</tr>
</tbody>
</table>

Table 5.14: The heat treatments performed on the studied steels

<table>
<thead>
<tr>
<th>Austenitizing</th>
<th>Quenching</th>
<th>Tempering</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>Time (h)</td>
<td>Temperature (°C)</td>
</tr>
<tr>
<td>Z-Nb</td>
<td>1150</td>
<td>1</td>
</tr>
<tr>
<td>TAF B</td>
<td>1150</td>
<td>1</td>
</tr>
<tr>
<td>FT3B</td>
<td>1150</td>
<td>1</td>
</tr>
<tr>
<td>Mat-B</td>
<td>1100</td>
<td>1</td>
</tr>
</tbody>
</table>

Specimen preparation for atom probe tomography

Both the conventional two-step electropolishing method and in-situ lift out in FIB/SEM were used to prepare APT specimens. For electropolishing, the details were reported previously [11]. In order to perform APT analyses of boron at prior austenite grain boundaries (PAGBs), the in-situ lift-out technique was used. The sample was first mechanically polished, cut to a disk 3 mm in diameter and 50 μm in thickness, and then electropolished with a solution of 10% perchloric acid in ethanol.
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Figure 5.47: SEM secondary electron micrograph, showing the typical microstructure of 9–12% Cr steel. Precipitates (bright contrast) heavily decorate prior austenite grain boundaries (highlighted with arrows) and martensite lath boundaries.

At the temperature of 240 K and voltage of about 21–23 V using a Struers “Tenupol-5” equipment (StruersApS, Ballerup, Denmark). The obtained smooth surface is less corroded compared to the surface by chemical etching; and it can easily reveal crystallographic information in the microscope. Site-specific APT specimens containing PAGBs were prepared in an FEI Helios NanoLab 600 FIB/SEM workstation (ThermoFisher Scientific, Oregon, USA) equipped with an electron backscatter diffraction (EBSD) (Oxford Instruments plc, Abingdon, UK) unit for TKD analysis. In order to identify the PAGBs, instead of using EBSD, like e.g. [2], a relatively high ion current (0.44 nA) was used to scan a large surface area, while simultaneous imaging. The obtained image clearly revealed the microstructure features like PAGBs due to the so-called ion tunnelling contrast. TKD mapping was used to guide ion milling of the APT tip: the starting step size for mapping was 100 nm, when the PAGB was far away from the APT tip apex; and the final step size was 10 nm, when the PAGB was close to the APT tip apex. Note, most of the APT results reported in this work were obtained from specimens prepared using the electropolishing method.

Atom probe tomography

A LEAP 3000X HR local electrode atom probe instrument (CAMECA, Gennevilliers Cedex, France) was used. The specimen temperature during analysis was in the range of 55–65 K. Laser (green, wavelength
532 nm) pulsing mode was used, with a frequency of 200 kHz, and a laser energy of 0.3 nJ. The chosen target evaporation rate was 0.5–2%. The acquired data were further analysed by using the IVASTM 3.6.10 software developed by CAMECA.

5.5.2 Results

General microstructure of 9–12% Cr steels

All the 9–12% Cr steels studied in this paper exhibit a typical lath martensitic structure, consisting of prior austenite grains (tens of micrometers in size), subdivided into blocks, which consists of packets of elongated laths (hundreds of nanometers in width, and tens of micrometers in length) and precipitates (from a few nanometers to a few micrometers). The precipitates, mainly carbides directly after tempering, and Laves phase after long term aging or creep testing, decorate mainly PAGBs and lath boundaries. During chemical etching, the steel matrix was preferentially etched away, giving a gray contrast in the SEM secondary electron image, while the precipitates were left intact above the surface, giving a bright contrast (Figure 5.47).

A novel and convenient method for preparing boundary-containing specimens

In order to conveniently prepare APT specimens containing a specific PAGB, a novel custom-designed flip-out sample holder was made, which can flip between 0 and 90° (Figure 5.48). The current specimen preparation method (illustrated in Figure 5.49 (a)-(f)) is different from the conventional procedure in a few aspects: the PAGBs were identified by ion tunnelling imaging in the FIB mode (Figure 5.49 (a)); the lift-out piece containing the PAGB was attached to a pre-sharpened needle mounted on the flip holder at the 0° position, using Pt deposition to weld (Figure 5.49 (d)); the holder was flipped to the 90° position, and the tip was annularly milled until the final radius of the specimen tip was less than 50 nm (Figure 5.49 (f)). Ion milling was gradually performed, guided by TKD mapping. When the PAGB reached a distance of less than 1 µm from the apex, the progress was checked using TKD every 5 seconds of milling until the boundary was located within 100 nm of
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Figure 5.48: Custom-designed holder with the flip-out mechanism for convenient site-specific APT specimen preparation: (a) in horizontal (0°), (b) in vertical (90°) position.

the APT tip. Additionally, TKD was also used for identifying the exact GB misorientation. The TKD map shows the relative position of the boundary to the APT tip apex (Figure 5.50).

Boron at boundaries

The segregation of various elements to the boundaries in 9–12% Cr steels with different thermal conditions shows an interesting trend in the width of the concentration profiles, and the position of the peak concentration. In order to obtain the concentration profiles, a cylinder 15 nm in diameter was defined and placed carefully, so that it goes perpendicularly through the boundary. For clear visibility, only the concentration profiles of B together with Cr, and B together with C, were plotted. In general, since the steels had not reached their equilibrium state after tempering or short-term aging, a significant part of the segregation is non-equilibrium in nature, which is reflected by the wider segregation profiles. One typical example is a Z-phase strengthened experimental steel, Z_Nb with a low C concentration (50 ppm) and 40 ppm B, which was tempered at 650°C for 24 h [12, 13]. Note, due to the low C concentration (0.005 wt.% vs. ≥0.14 wt.%), no M23C6 carbides were observed; and M23C6 can dissolve quite some boron (see next sub-section). Hence, much of the B atoms are available to segregate to lath boundaries. The plane of the boundary is at an angle of 60° to the analysis axis (inset Figure 5.51(a)).

The full width at half maximum (FWHM) of the Cr and B profiles
**Figure 5.49:** Site-specific sample preparation for APT specimens containing a prior austenite grain boundary (PAGB). (a) Identify PAGBs by ion tunnelling in FIB; (b) Select and mark the PAGB by slight milling; (c) Lift-out the specimen piece with the microprobe; (d) Attach the specimen piece onto a needle in the custom-made sample holder; (e) Tilt the specimen $90^\circ$ for the final annular milling; (f) A final APT tip containing the PAGB.

**Figure 5.50:** A TKD map of a sharpened APT specimen, and the corresponding profile of misorientation in relation to the position from the apex of the APT specimen.
5.5 Analysing boron in 9–12% chromium steels using atom probe tomography

is 7.1 and 9.0 nm, respectively (Figure 5.51 (a)). Since the C concentration is rather low and scattered much, it is difficult to determine its FWHM. However, the profile of B is obviously wider than that of C. Additionally, the peak of the B profile comes ahead of the peak of C (Figure 5.51 (b)). For a specimen made from a high B concentration (300 ppm) experimental steel, TAF B, aged at 650° for 27,000 h, it contains a boundary plane at an angle of 45° to the analysis axis (inset Figure 5.51 (c)). The FWHM of the Cr and B profiles is 2.5 and 6.4 nm, respectively (Figure 5.51 (c)). The width of the B profile is slightly wider than that of C (Figure 5.51 (d)). For the same material with the same thermal condition, however, a boundary perpendicular to the analysis axis (inset Figure 5.51 (e)), the FWHM of Cr and B profiles is 1.5 and 5.2 nm, respectively (Figure 5.51 (e)). Again, the profile of B is wider than that of C; the peak of the Cr profile comes ahead of B, which, in turn, comes ahead of C (Figure 5.51 (e) and (f)). Although within this study, we developed a novel method for APT specimen preparation containing PAGBs, it is worth noticing that here all the specimens were prepared using the electropolishing method.

Thus, it is difficult to identify the type of the boundaries, i.e., PAGB or lath boundary. However, by analysing the crystallographic pole regions in the APT reconstruction using iso-concentration surface based on the ion density, it was indicated that the first boundary was a lath boundary with a continuous pole column. Additionally, this boundary was extracted from a much larger reconstruction volume, which contains two parallel boundaries with similar boron enrichment. The second and third boundaries were most likely PAGBs or block boundaries with discontinuous pole columns across the boundaries.

**Boron in precipitates**

In order to understand the field evaporation behaviour of B as a diluted solute in precipitates, an APT data set containing two Cr-rich M$_{23}$C$_6$ (M = Cr, Fe, Mo) precipitates with three interfaces were analysed in detail: upper interface (using the direction of APT analysis as reference; the angle between the plane and the analysis axis 45°), lower interface (60°), and parallel interface (0°) (inset of Figure 5.52 (a)). The APT tip was made from another high B concentration (250 ppm) experimental steel, FT3B, under the as-tempered condition. Since the interfaces
Figure 5.51: Boron together with chromium and boron together with carbon concentration profiles across boundaries in different types of steels with different thermal history: a) Z_{CrNbN} and b) tempered at 650 °C for 24 h, with the boundary at 60° to the analysis axis; c) and d) TAF B aged for 27,000 h, with the boundary at 45° to the analysis axis; e) and f) TAF B aged for 27,000 h, with the boundary perpendicular to the analysis axis. Insets are atom maps, showing the analysed grain boundaries.
are rather irregularly curved, in order to ensure that the concentration profiles were obtained from volumes perpendicular to the interface, the embedded function in the IVAS software – proxigram – was used. After defining an iso-concentration surface, this function defines small volumes perpendicular to the surface (note, the calculation is based on the smallest volume unit – voxel), and then integrates along the entire surface. In contrast, manual operation defines a small cylinder and adjusts its position until “perpendicular” to the interface by the operator, which is often inaccurate, and thus the interface concentration is easily smeared. In order to obtain a proxigram for each of the interfaces, three sub-volumes were cut and extracted, and each sub-volume contains only one of the above mentioned interfaces. Then the proxigrams were obtained based on the iso-concentration surface for 35 at% Cr. In the proxigrams, the transition region from the matrix to the precipitates is the widest for the parallel interface (0°) followed by the upper interface (45°) and the lower interface (60°) (Figure 5.52 (a), only the Cr profile of the parallel and lower interface were plotted). The maximum value of the first derivative of the curve is 18 at%/nm for the parallel interface, and 52 at%/nm for the lower interface. Additionally, an interesting trend exhibits in the Cr and B profile for interfaces positioned differently in relation to the analysis axis: for the parallel interface, the B and Cr profiles deviate slightly (Figure 5.52 (b)); for the upper interface, the B and Cr profiles matches each other rather well, (Figure 5.52 (c)); for the lower interface, the trend of B and Cr profiles deviate from each other the most (Figure 5.52 (d)). However, in all cases, the boron profile is wider than that of chromium.

In order to understand the field evaporation behaviour of B in borides, an APT data set containing a M₂B (M = Cr, Fe and Mo) \[14\] formed in as-quenched Mat-B, the 10% Cr commercial steel, was analysed. This boride is located at a PAGB, which was extracted in the FIB/SEM using the novel specimen preparation method. Proxigrams of the upper (\(~80°\)) and lower (\(~90°\)) interfaces (inset Figure 5.53 (a)) of the M₂B, are shown in Figure 5.53 (a) and (b), respectively. The data set was first subdivided into two volumes, one contains only the upper interface, and the other contains only the lower interface. The proxigrams were then defined by the iso-concentration surface of 29% B. Interestingly, the Cr profile is wider for the upper interface, while the B profile is slightly
Figure 5.52: Proxigram of carbide M₂₃C₆; the iso-concentration surfaces was defined by 35% Cr. a) Comparison between the Cr profile for the parallel and the lower interface; the transient region from the steel matrix to the carbide is wider for the parallel surface; b) For the interface parallel to the analysis axis (0°), the shape of the B and Cr profiles deviates slightly; c) For the upper interface (45°), the shape of B and Cr profiles fits well; d) For the lower interface (60°), the shape of B and Cr profiles is different, the B profile is wider than that of Cr. Inset, showing the analysed iso-concentration surfaces.
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Figure 5.53: Proxigram of a boride $M_2B$; the iso-concentration surface was defined by 29% B. a) For the upper interface of the boride, the profile of B is slightly narrower than that of Cr; b) For the lower interface, the profile of B is slightly wider than that of Cr. Inset, showing the analysed boride.

Quantification of boron in borides

When analysing borides with APT, in this case a $M_3B_2$ ($M$=Mo, Fe, Cr, V, and Nb) formed in TAF B as-tempered, a large portion of the detected field evaporation events is multiple events, accounting for 40%, while almost all the rest are single events, only 0.2% unidentified events. This type of borides is the equilibrium phase formed at high temperatures, and was identified by electron diffraction in a steel with similar boron concentration and heat treatment conditions [15]. Their chemical composition is expected to be stoichiometry. As a comparison, for the steel matrix, the multiple events only account for less than 5% when laser pulsing is used. The mass spectra for single and multiple events are presented in Figures 5.54 (a) and (b), respectively. For individual elements, the ratio between the total single to multiple events varies largely: C 0.45, B 0.54, Mn 1.7, Mo 2.5, Nb 2.6, Cr 2.9, V 3.0 and Fe 4.0. These numbers indicate that C and B field evaporated preferentially as multiple events, while the metallic atoms evaporated mostly as single events. Interestingly, the species that are likely originated from the residual gas in the vacuum system: i.e., $H^+$, $H_2^+$, $O^+$, and $OH^+$, were predominately found in the single event spectrum (Figures 5.54 (a)).

Compared to the natural abundance ratio between the minor (10B)
and major (11B) isotope for boron (19.82% and 80.18%) [16], all the minor 10B peaks at mass-to-charge ratio 3.3, 5, and 10 Da were higher than the expected value, mainly due to the effect of dead-time in the detector. Not surprisingly, for single-event ions the abundance is very close to their natural abundance: 80.5±0.4% for 11B+ at 11Da, and 80.9±0.4% for 11B2+ at 5.5Da; while for multiple-event ions the abundance deviates much from their natural abundance: 76.0±0.3% for 11B+ at 11Da, and 75.2±0.3% 11B2± at 5.5Da.

By counting just the ions from the spectrum, the B concentration was calculated as 36.5%. Therefore, we propose a simple two-step correction: firstly based on the less affected and more accurate isotope 10B:

\[
corr^{10}B = orig^{11}B \times \frac{80.18\%}{19.82\%},
\]

secondly based on the calculated ion loss at 11B: loss\textsuperscript{11}B = corr\textsuperscript{11}B - orig\textsuperscript{11}B to estimate ion loss at isotope 10B:

\[
loss^{10}B = loss^{11}B \times \left(\frac{19.82\%}{80.18\%}\right)^2,
\]

Note: the square of the constant term is stemmed from the possibility that two 10B and two 11B hit the detector simultaneously, which is the reason behind the loss in B ions. After the two step correction, the B concentration was calculated as 39.8%; by adding C (0.11%), the total anion concentration is 39.9%, very close to the stoichiometric value 40%.

### 5.5.3 Discussions

**APT specimen containing a PAGB**

Preparation of APT specimens containing PAGBs has been a challenge. Using the electropolishing technique, Karlson and Norden systematically analysed B segregation in austenitic steels, iterating back-polishing and checking in a TEM by imaging until the grain boundary was <100 nm from the specimen apex [17]. However, this technique is not applicable to 9–12% Cr steels, since the large number of lath boundaries interfere with the relatively few PAGBs. The FIB/SEM lift-out technique makes the preparation of APT specimens containing PAGBs in 9–12% Cr steels
Figure 5.54: Mass spectra for a boride $M_3B_2$. a) Single hits showing a higher background level; b) Multiple hits showing much lower background level.
routinely feasible. For lift-out specimens, two types of geometries are possible: the PAGB runs approximately parallel to the axis of the cone of the APT specimen [2, 18], or approximately perpendicular to the axis, as the current study. For the former geometry, the success rate of obtaining a final APT tip containing the selected PAGB turned out to be rather low for the 9-12% Cr steels that we studied, since for PAGBs the misorientation angles between the neighbouring grains are often high. Consequently, the two grains often behaved very differently during ion milling, which was detrimental to the quality of the final APT specimens. While for the latter type of geometry, although so far we have only achieved one APT tip containing the PAGB since we used a single needle in the flip holder, the process is relatively easy to control, thus ensuring a much higher success rate. Additionally, the flip-out specimen holder makes the lift-out procedure with the perpendicular geometry convenient. Finally, compared to the pre-manufactured Si chip for APT specimens, the single wire specimen enables TKD analysis, which provides complementary information on crystallography to the chemical information obtained from APT [19, 20, 21]. Further improvement on the throughput can be achieved by broadening the lift-out piece so that it can yield several APT tips, and, instead of a single needle, using an electropolished TEM grid with several needles to support the tips.

**Distribution of boron concentration profiles**

B and C have a higher evaporation field, compared to the metallic elements in the steels, such as Fe and Cr [8]. Therefore, they often exhibit preferential retention [22, 23], trajectory aberration [24], and ion pile-up effects on the detector [10]. First we discuss the effect of retention. During APT analysis, surface atoms with preferential retention tend to be delayed in ion evaporation, which may affect chemical analyses of steels [25]. Additionally, the B profiles for the interfaces are expected to shift slightly after the Cr profile, e.g., Figure 5.53 (a), an almost perpendicular upper interface, and Figure 5.52 (d) and 5.53 (b), almost perpendicular lower interfaces. Even the peaks of the concentration profiles for boundaries show the same trend, e.g., Figure 5.51 (e) and (f). Finally, the asymmetric shape of the boron segregation profiles (Fig 5.51 (a), (c) and (e)), is also attributed to preferential retention. At the same time, trajectory effect also plays a role. It was shown by simulation that
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for grain boundaries parallel to the analysis axis, the profile for atoms with higher evaporation field are broadened \[26]\. In this study, it was found that for the boundaries the B profile is always wider than the Cr profile (Figure 5.51 (a)); it is true even for the interfaces of precipitate/matrix, particularly for the ones that are parallel to the analysis axis (Figure 5.52 (b)). Interestingly, if only counting the effect of retention, the upper interface (\(\sim 45^\circ\) to the analysis axis) in Figure 5.52 (c), would have a slightly shifted Cr profile ahead of the B profile. However, due to the trajectory effect, the profile of B becomes slightly wider than that of Cr. Indeed, the trajectory effect is most significant in the XY plane, i.e., for plane features parallel (Figure 5.52 (a)) or at a relatively small angle to the analysis axis; and is less significant in the Z direction, i.e., for plane features perpendicular to the analysis axis (Figure 5.51 (e) and (f)). Therefore, in order to mitigate the phenomena stemmed from the trajectory aberration and preferential retention, it is recommended to prepare specimens that can sub-cut the upper interfaces that are positioned roughly perpendicular to the analysis axis, and analyse the sub-cut interfaces separately.

There are two different segregation behaviours, equilibrium and non-equilibrium segregation. Besides the thermodynamic criteria, which can be checked using carefully designed heat treatment conditions \[27, 28]\, the width of the distribution of segregated atoms also provides an important clue on the segregation mechanisms, indicating the type of segregation and diffusion of vacancies and solute complexes \[29]\. Although a series of systemically designed heat treatment conditions on one steel is needed to understand the segregation mechanisms, which is out of the scope of the present study, it is interesting to note that i) the distribution of segregated elements varies largely: wide distribution of Cr \(\sim 5\) nm, in Z-Nb steel quenched and aged at 650 °C for 24 h (Figure 5.51 (a)), and narrow distribution of Cr \(\sim 2\) nm, in TAFB steel aged at 650 °C for 27,000 h (Figure 5.51 (c) and (e)); and ii) B profiles are generally wider than Cr profiles. Although preferential retention may cause widening of the B profiles, comparing to the profiles of C (particularly, Figure 5.51 (e)), which has an even higher evaporation field, the wide B profile seems to partially reflect the real B distribution. APT has been proven a very powerful tool to understand the mechanisms of B segregation, e.g., \[2, 14, 29, 30]\, however, remarkable discrepancies were found
between the experimental results and theoretical prediction, thus further work combining experiment and theory is required to gain a better understanding.

**Quantification of boron in borides**

When analysing borides, a large number of the field evaporation events are multiple events, in particular for boron. When more than two B ions of the same type hit the micro channel plate detector very close in time and space, the ions are recorded as a single ion, due to the limited capability of the detector to identify multiple hits [31]. This limitation often leads to an underestimation of the B concentration. A similar issue is frequently observed for carbon in carbides; a correction based on the minor isotope 13C was proposed [32]. Since the probability of two 13C (natural abundance: 1.07%) ions hit the detector simultaneously is much lower compared to that of two 12C (98.93%), the minor isotope suffers significantly less from the multiple events. Satisfactory results on quantifying various carbides were obtained. The situation for B is more complex: its minor isotope 10B corresponds to 19.82%, which is remarkably larger than that of carbon 1.07%. Therefore, a two-step correction was proposed: first a correction on 11B based on the minor isotope 10B is performed; a further correction is then performed based on the recovered 11B. The method can be iterated several times, and will yield a stable corrected value (in this particular case six times). However, the first round contributes most to correction.

**5.5.4 Conclusions**

Boron, either segregated at boundaries or dissolved in precipitates in several 9–12% Cr steels, were analysed using APT.

- A novel APT specimen preparation method was developed for convenient lift-out of PAGB-containing specimens, using a customer-designed flip-out APT specimen holder, which enabled TKD to monitor the procedure. The PAGB is located approximately perpendicular to the axis of the APT specimen.

- B has a high evaporation field compared to the steel matrix. In order to mitigate the effects that stem from trajectory aberration
and preferential retention, we recommend to prepare APT specimens with the upper interface positioned roughly perpendicular to the analysis axis; under reconstruction, we recommend to sub-cut the upper interface, and analyze the sub-cut interface separately.

- Quantification of B in borides is negatively influenced by the large portion of multiple events. A two-step correction based on the 10B isotope can be used to achieve good quantification.

### 5.5.5 Acknowledgments

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### Bibliography


Chapter 6

Discussion

This chapter provides a general discussion of the included papers and manuscripts based on important findings and conclusions. For the detailed discussion of each individual manuscript, the reader is referred to the chapter “Results”.

6.1 Development of 11.5% Cr low nitrogen martensitic steel

Results, obtained in the present PhD work showed that in order to increase corrosion resistance by increasing Cr content in martensitic steels and maintain microstructure stability, the right balance between Cr, B, V, Nb and in particular N and Ti should be chosen. The Belgorod alloy with 10% Cr, B and low N, which had shown the best creep stability until now, was taken as the initial alloy composition in the present work. However, the alloy B0 intended to copy the Belgorod alloy showed very poor creep stability at 650 °C event though the coarsening stability of $\text{M}_2\text{C}_6$ carbides in the B0 was similar to the Belgorod alloy. Instead it was found that all notrogen in the B0 was tied up in TiN, which was not the case for the Belgorod alloy. In the 11.5% Cr alloy B1 nitrogen was also tied up as TiN and it showed similar poor creep strength as the B0.

The 11.2% Cr alloys SST1 and SST2 had free nitrogen available after formation of TiN, and this lead to formation of Z-phase and breakdown in creep strength after 3,000-5,000 h at 650 °C. Delayed Z-phase forma-
tion in the 10% Cr Belgorod alloy is believed to explain high long-term creep stability of this alloy.

It is speculated that the low (free) nitrogen content in the Belgorod and SST steels can result in the formation of extremely fine VN precipitates as observed in literature. This would explain the high creep strength of the 10% Cr Belgorod alloy and the breakdown of the 11.2% Cr SST alloys, since the VN precipitation strength is lost by the formation of the small volume fraction of Z-phase observed in the SST steels. Fine VN precipitates are not visible with the TEM microscope techniques applied here.

6.2 High Cr steels alloyed with boron

Addition of small amounts of boron in the steel composition has been known as another effective method to increase creep stability of 9-12% Cr martensitic steels. The beneficial effect of boron has been explained by the incorporation boron in $M_{23}C_6$ carbides forming $M_{23}(C,B)_6$ borocarbides, thus, reducing their coarsening rate during microstructure evolution. The mechanisms of reducing the coarsening rate of the borocarbides as well as boron behaviour in this process are still not well understood. However, it is clear that boron should be added to steel in an optimal balance along with other alloying elements. Thus, extensive boron and nitrogen contents lead to the precipitation of coarse BN nitrides, which is considered as a harmful phase. The influence and behaviour of other alloying elements are very important for creep stability of boron-added martensitic steels. In the present work the behavior of boron during normalizing of 9-10% Cr steels was studied by atom probe tomography (APT) to improve the general understanding of this element.

Three 9-10% Cr martensitic steels with 10, 70 and 100 ppm of boron were investigated. Boron segregated to austenite grain boundaries during cooling but unlike the behavior in low alloy martensitic steels where all boron segregates, significant amounts (20-30%) of the added boron is left unsegregated in the 9-10% Cr steels. APT results indicate that the segregated boron concentration on austenite grain boundaries saturate at 0.8 at.% in the 9-10% Cr steels with up to 70 ppm of boron. At more than 100 ppm boron content, fine borides of type $M_2B$ form on austenite
grain boundaries during cooling. It is uncertain how these fine borides interact with M$_{23}$C$_6$ carbides, which precipitate during subsequent tempering.

Half (45-55%) of the added boron to the 10 ppm and 70 ppm steel was accounted for by the APT measurements, and the remaining is found as BN in the 10 ppm steel. Large BN was also found in the 100 ppm boron steel, but the remaining boron in the 70 ppm steel could not be located.

The measured concentration profiles at austenite grain boundaries of the 10 ppm and 70 ppm steels did not fit well to theoretical predictions. For diffusion limited equilibrium segregation wide low boron concentration diffusion zone should develop according to theory, but this was not observed. For non-equilibrium segregation models fail to predict the high local concentration at grain boundaries. Thus more complicated models are required to determine the prevailing segregation mechanism for boron in the 9-12% Cr steels.
Chapter 7

Conclusion

The aim of the present work was to study alloying concepts for stable martensitic creep resistant 11-12% Cr steels aimed to be stronger and more corrosion resistant than currently available 9-10% Cr steels. Four 10-11.5% Cr steels with boron additions and with low nitrogen content balanced by titanium were studied in terms of microstructure stability, creep resistance and precipitate evolution.

In addition, a general study on boron behavior in 9-10% Cr steels was initiated in the present project and lays the foundation for further research on this topic aiming to optimize boron additions to the 9-12% Cr creep resistant steels.

Details on experimental results as well as new observations and findings of the present dissertation can be found in the individual result chapters. The key conclusions of the work are:

- Four 10-11.2% Cr boron-added martensitic steels with varying contents of titanium and nitrogen were investigated. None of the investigated steels reached the expected high creep strength and long-term microstructure stability.

- Detailed characterization of microstructures with transmission electron microscopy (TEM) indicated rather similar stability of M$_{23}$C$_6$ carbides in the steels even though large scatter in creep strength was observed.

- Slight differences in the contents of titanium and nitrogen led to large differences in creep strength. The 10% Cr and 11.5% Cr
steels, in which all nitrogen is tied up as TiN, showed low strength, whereas two 11.2% Cr steels with free nitrogen available after formation of TiN showed high creep strength up to 3,000-5,000 h at 650 °C.

- Z-phase formation was observed after isothermal ageing for 5,000 h at 650 °C in the 11.2% Cr steel with the highest amount of free nitrogen after TiN formation. The 11.2% Cr steel with lower amount of free nitrogen showed no Z-phase formation after isothermal ageing up to 10,000 h, but creep accelerated Z-phase formation was observed after 5,000 h at 120 MPa/650 °C.

- It is speculated that extremely fine nitrides (presumably VN) can form in steels with low amounts of free nitrogen after TiN formation. In steels with 11.2% Cr the fine nitrides transform to Z-phase rather quickly, whereas in steels with 10% Cr they can provide long-term creep stability.

- Boron behavior was investigated by atom probe tomography in three martensitic 9-10% Cr steels with boron contents of 10 ppm, 70 ppm and 100 ppm. In all steels boron segregated to austenite grain boundaries during air cooling from 1100 °C. Similar grain boundary concentrations (0.8 at.%) were found in the 10 ppm and 70 ppm boron steels.

- In the 100 ppm boron steel fine M$_2$B borides (15 x 70 nm) were found to precipitate on some of the austenite grain boundaries during cooling form 1100 °C. No such borides were observed in the steels with lower boron content.

- Significant amounts of non-segregated boron remains in the center of grains after normalization in all steels. About half (45-55%) of the added boron to the 10 ppm and 70 ppm steels could be located by based on the APT measurements. In the 10 ppm boron steel the boron not accounted for could be located in boronitrides. The 70 ppm boron steel contains titanium and no free nitrogen is available for boronitride formation.
Chapter 8

Further work

In the present PhD work promising approaches for the alloy development of 9-12% Cr martensitic steels with improved microstructure stability were investigated. In addition new findings in the microstructures of studied 9-12% Cr martensitic steels were revealed.

The work showed that during tempering at 650 °C denuded zones a few µm wide formed on the PAGBs in the 11.2% Cr martensitic steels. However, the nature of this phenomenon, its effect on the mechanical properties during further exposure at 650 °C as well as methods for avoiding the formation of the precipitate-free zones were not studied in the present project due to time limitations. This phenomenon should be analysed further in future studies.

Microstructure characterizations of new experimental 11% Cr martensitic steels using TEM have not detected the presence of V-rich carbonitrides of MX type, which are often found in 9% Cr martensitic steels. It was assumed that V-rich (carbo)nitrides nucleate as extremely small particles (few nanometers in size) which could not be detected with the applied TEM techniques. APT and high resolution TEM should be used in order to check the presence of small V carbonitrides and the concentration of available V in the martensite matrix.

Fine (Cr, Fe)2B borides formed during cooling from normalization temperature were found for the first time in the 10% Cr martensitic steel. It was found that their presence and size are highly dependent on the cooling rate and boron concentration in the steel. Further, the role of these borides in the microstructure stability during high temperature
exposure and their effect on the formation and growth of the B-rich Cr carbides (Cr$_{23}$(C,B)$_6$) should be investigated in detail. Complementary work, such as analysis of the influence of different HTs (normalization temperature, cooling rate, tempering) could reveal the role of the fine borides in microstructure stability.

The study of boron presented in the PhD work was our first results and attempt to get better understanding of its behaviour in 9-10% Cr martensitic steels. This study should be extended by investigating different alloys comprising various boron concentrations, normalization temperatures and cooling rates. Based on experimental data from different boron containing alloys, thermodynamic and kinetic models for predicting the boron behaviour in steels should be created.
## List of Acronyms

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>APT</td>
<td>Atom probe tomography</td>
</tr>
<tr>
<td>AP</td>
<td>Atom probe</td>
</tr>
<tr>
<td>CCD</td>
<td>Couple-charged device</td>
</tr>
<tr>
<td>EBSD</td>
<td>Electron backscatter diffraction</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>EM</td>
<td>Electron microscopy</td>
</tr>
<tr>
<td>EELS</td>
<td>Electron energy loss spectroscopy</td>
</tr>
<tr>
<td>FCC</td>
<td>Face-centered cubic</td>
</tr>
<tr>
<td>FIB</td>
<td>Focus ion beam</td>
</tr>
<tr>
<td>GB</td>
<td>Grain boundary</td>
</tr>
<tr>
<td>HT</td>
<td>Heat treatment</td>
</tr>
<tr>
<td>LOM</td>
<td>Light optical microscopy</td>
</tr>
<tr>
<td>PAGB</td>
<td>Prior austenite grain boundary</td>
</tr>
<tr>
<td>PTA</td>
<td>Particle tracking autoradiography</td>
</tr>
<tr>
<td>UTS</td>
<td>Ultimate tensile strength</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SIMS</td>
<td>Secondary ion mass spectroscopy</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>------------------------------------</td>
</tr>
<tr>
<td>TKD</td>
<td>Transmission kikuchi diffraction</td>
</tr>
<tr>
<td>CCT</td>
<td>Continuous cooling transformation</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
</tbody>
</table>
Appendices
Appendix A

ECCC conference paper
On the non-equilibrium segregation of boron in 9-12%Cr steels

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Summary
The addition of only 20-150 ppm of boron to martensitic 9-12%Cr steels has a strong enhancing effect on their creep strength, and boron-added martensitic creep strength enhanced steels have been introduced in power plant constructions. Boron is found to redistribute in the martensitic steels during cooling after normalizing in a non-equilibrium segregation process. In this work we attempt to quantify boron segregation during solution treatment in a martensitic 9%Cr steel containing 108 ppm of boron by atom probe tomography and transmission electron microscopy. The investigated material was solution treated at 1100°C for 1 h and cooled in air. Plate-like boride of CrB was found on a prior austenite grain boundary (PAGB). The distribution of B, Cr, Fe, Co, Mo, C and other elements in boride and matrix was quantified. Boron is considered to segregate onto PAGBs by non-equilibrium mechanism.

Key Words
Martensitic creep resistant steels, boron, non-equilibrium segregation, atom probe tomography.

Introduction
Martensitic steels with 9-12%Cr are extensively used as construction materials for boilers, steam pipes and turbines working at elevated temperatures in steam power plants. Modern creep strength enhanced grades such as the 91, 92 and FB2 allow operation at steam temperature up to 600-620°C. They are 9% CrMo/W steels with additions of V, Nb and N for precipitation hardening by fine (V,Nb) nitrides. Above 620°C, the 9% chromium provides in sufficient oxidation resistance, and an increase of the chromium content up to 11-12% is required in order to increase the operating temperature. However, increased chromium contents in such steels have been found to accelerate formation of Cr(V,Nb)N Z-phases and dissolution of the strengthening (V,Nb)N nitrides, and this causes breakdown in the long-term creep strength [1-4]. Thus, an increase of the Cr content from 9 to 11-12% Cr requires new alloy design concepts, which cannot rely extensively on (V,Nb)N strengthening.

Since the martensitic creep resistant steels are extremely complex alloys, new alloy concepts need to be based on deep understanding of the role of individual alloying elements in the 9-12%Cr steels. In the present article we focus on the understanding of boron, which has provided improved creep strength in a number of steels, including the commercial grades 92 and FB2 as well as several experimental alloys. Even though boron is widely used there is still a lack of detailed understanding of its behavior in the steels and the mechanism by which it strengthens them. This means that our ability to control and optimize boron alloying is limited.

Boron alloyed 9-12%Cr steels
The strong enhancing effect of boron on creep strength of martensitic 9-12%Cr steels was first seen by Fujita in the 1950’s. His pioneering work resulted in the TAF steel, which is still among the strongest martensitic creep resistant steels tested so far [5]. The relatively high boron content of 400 ppm in the steel led to problems with manufacturing of large components, and the steel was never put into practical use. However, the results from the TAF were implemented from the middle of the 1980’s in the steel Grade 92, which was the first standardized martensitic creep resistant steel alloyed with boron [6].

The European COST Actions investigated boron alloyed steels for turbine rotors and casings from the early 1980’s, at first with the steel B, which was derived from the TAF steel [7]. Later, steel B was optimized - mainly by Co addition - to the grades FB2 and CB2 for forgings and castings. These are currently the strongest steels available for advanced steam turbines [8].

From the beginning of this century systematic studies of effects of boron and nitrogen on the creep properties of 9%Cr3Co3W steels were carried out at NIMS in Japan. This led to the MARB and MARBN type steels, which...
achieve high creep strength either by addition of boron alone or by addition of boron together with limitations on the nitrogen content to around 100 ppm. The optimized B and N levels in the MARBN steels prevent the precipitation of BN particles, which reduce the content of boron and nitrogen available for strengthening [9].

Positive effects on creep rupture strength by boron additions to the 9Cr1Mo steel Grade 91 have been shown by researchers from India [10].

Recently, Mishnev et al. used boron together with reduced nitrogen content down to 30 ppm in a 10%CrMoW steel, which showed high creep stability, leading for the first time to clearly higher creep strength than the TAF steel [11,12].

Table 1 shows typical chemical compositions and heat treatments of some of the discussed alloys, and figure 1 shows their creep rupture strength at 650ºC. It is clear that boron additions and reduced nitrogen can provide strength improvements close to the dream target of 100 MPa for 10^5 hours at 650ºC. However, none of the investigated steels have sufficient Cr content to provide the required oxidation resistance.

Table 1. Typical chemical compositions (Mass%, bal. Fe) and heat treatments of some of the discussed steels

<table>
<thead>
<tr>
<th>Steel</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Mo</th>
<th>W</th>
<th>Ni</th>
<th>Co</th>
<th>V</th>
<th>Nb</th>
<th>Ti</th>
<th>N</th>
<th>B</th>
<th>Norm. Temp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TAF</td>
<td>0.18</td>
<td>0.50</td>
<td>1.0</td>
<td>0.5</td>
<td>1.5</td>
<td>0.1</td>
<td>-</td>
<td>0.2</td>
<td>0.15</td>
<td>-</td>
<td>0.01</td>
<td>0.0400</td>
<td>1150ºC 700ºC</td>
<td></td>
</tr>
<tr>
<td>P92</td>
<td>0.11</td>
<td>0.10</td>
<td>0.45</td>
<td>8.82</td>
<td>0.47</td>
<td>1.87</td>
<td>0.17</td>
<td>-</td>
<td>0.19</td>
<td>0.06</td>
<td>-</td>
<td>0.047</td>
<td>0.0020</td>
<td>1070ºC 780ºC</td>
</tr>
<tr>
<td>MARBN</td>
<td>0.08</td>
<td>0.3</td>
<td>0.5</td>
<td>9.1</td>
<td></td>
<td></td>
<td></td>
<td>0.21</td>
<td>0.55</td>
<td>-</td>
<td>0.01</td>
<td>0.0110</td>
<td>1150ºC 770ºC</td>
<td></td>
</tr>
<tr>
<td>Belgorod</td>
<td>0.10</td>
<td>0.06</td>
<td>0.10</td>
<td>10.0</td>
<td>0.70</td>
<td>2.0</td>
<td>0.17</td>
<td>0.60</td>
<td>0.30</td>
<td>0.05</td>
<td>0.003</td>
<td>0.0080</td>
<td>1060ºC 770ºC</td>
<td></td>
</tr>
</tbody>
</table>

Figure 1. Creep rupture test results at 650ºC of discussed steels.

Boron behavior in 9-12%Cr steels

- Nature of boron in steels
  Boron has been added to steels since the beginning of the last century to enhance strength and hardenability. Tremendous effects can be obtained for extremely low additions in the order of 5-30 ppm, but boron can also introduce ductility dips during manufacturing and unpredictable behavior during heat treatment. Thus boron has always been considered as a somewhat mysterious alloying element.
This special behavior is basically caused by a large misfit between the boron atom and the steel lattice in both substitutional and interstitial sites [13-19]. The size of a boron atom is larger than interstitial elements (e.g., C and N) but smaller than substitutional (e.g., Fe, Cr and Mo) [16]. This leads to a dual nature of boron, which was for long a source of controversy, since experimental data supported either the substitutional or the interstitial nature of boron in bcc-iron [17-22]. Substitutional solid solution was indicated by x-ray measurements, diffusion experiments, and internal friction measurements [18] while internal friction measurements confirmed an interstitial solid solution of boron in bcc-iron [18, 19]. The presence of B in both substitutional and interstitial sites was also detected [20-22]. In fact, depending on the energy benefit, boron atoms tend to transit from substitutional to interstitial sites, which can explain the dual nature of diffusion data for boron in steel [20]. This intermediate size of the boron atom gives it a strong tendency to segregate to lattice defects, phase interfaces and grain boundaries.

- **Boron containing precipitates**

  Boron containing precipitates in steels include borides, boro-nitrides and boro-carbides, see e.g. [17]. The beneficial effect of boron on creep strength of the martensitic 9-12%Cr steels is mainly attributed to a reduction of the coarsening of $M_2(C,B)_{3}$ boro-carbides in the steels, especially near the prior austenite grain boundaries [9, 23-25]. However, the mechanism for the reduced carbide coarsening remains unclear [26, 27].

  Boride phases, such as $M_2B$ and $M_2B_x$, where $M$ is mainly Fe, Cr, Mo and W, are most often unwanted in the 9-12%Cr steels since they form large particles on grain boundaries. These particles can lead to reduced toughness, and they do not provide significant precipitate strengthening. Thus, they reduce the effective boron content in the alloys. Coarse borides are considered to be formed during solidification, and they are normally not observed if the boron content is lower than $\sim$150 ppm [17].

  The boron nitride BN has received high attention in the 9-12%Cr steels recently. Research at NIMS indicated that the formation of BN tends to decrease the effective B and N available for $M_2(C,B)_{3}$ and MX precipitates, respectively. Coarse BN particles may be formed in steels with high B and N content, leading to embrittlement, whereas prevention of the formation of BN precipitates leads to high creep strength based on precipitate hardening from stable $M_2(C,B)_{3}$ as well as MX. This requires optimization of the balance of B/N concentrations by evaluation of the solubility product, equation 1, [28].

  \[
  \log \left[ \%B \right] = -2.45 \log \left[ \%N \right] - 6.81 \quad (1)
  \]

  The product is valid for 1050-1150°C where %B and %N are the soluble contents of boron and nitrogen in mass %.

  Finally, it should be mentioned that boron can stabilize low melting point phases at grain boundaries, which may lead to manufacturing difficulties during e.g. forging and welding.

**Non-equilibrium segregation of boron**

SIMS investigations of boron redistribution in steel P92 during normalizing and tempering heat treatments reveal that boron segregates to austenite grain boundaries during the normalizing heat treatment. During tempering, the boron redistributes into the grains within a few minutes, presumably to boro-carbides, figure 2 [25].

This indicates that boron distribution in the 9-12%Cr steels is governed by non-equilibrium segregation, which is well known from austenitic steels. This is a reasonable assumption, since the 9-12% Cr steels have an fcc lattice from the normalizing temperature and until the martensitic transformation. The non-equilibrium segregation occurs during cooling from the normalizing temperature by transport of boron-vacancy complexes to austenite grain boundaries [20, 29]. The cooling creates supersaturation of vacancies in the lattice, which annihilate at high angle grain boundaries and initiates a diffusion flow of vacancies towards the grain boundaries. Since boron segregates to vacancies, it is transported along with the vacancies to the grain boundaries, where the vacancies annihilate, leaving the boron atoms behind.

The phenomena of non-equilibrium segregation of B was first proposed by Westbrook in 1964 after observations of hardness increases in the vicinity of grain boundaries in non-ferrous alloys [30]. A few years later Aust [31] and Antony [32] established a model for the non-equilibrium segregation, which states that the mobility of the solute atom-vacancy complexes is higher than the mobility of solute atoms. Hence, the boron back-diffusion is slower than the
supply rate of new complexes, and the process maintains a boron flow into boundaries throughout the cooling. The model is based on the assumption that grain boundaries are effective sinks for vacancies.

Figure 2: SIMS boron micrographs of steel P92 (a) after hardening, tempered at 1023 K (750 °C) for (b) 0.5 min, (c) 1 min, (d) 1.5 min, and (e) 2 min [25].

Non-equilibrium segregation increases when cooling from higher normalizing temperatures, and in contrast to equilibrium segregation, which is localized to within a few atomic layers at the boundaries, the non-equilibrium segregation results in a much wider zone enriched by B [14, 33-35].

Influence of testing temperature and holding time on boron segregation has been studied for austenitic steels. It was found that the amount of non-equilibrium segregated boron is strongly dependent on the cooling rate, and it is largest at some intermediate cooling rate [13, 15, 19, 33, 36-39]. Boron segregation is strongest at the beginning of cooling when the temperature and atom mobility is highest [34].

Since non-equilibrium segregation appears to be the main process which determines the distribution of boron in the 9-12%Cr steels after normalizing and tempering, a detailed quantitative description of this process will be a key to the control and optimization of boron alloying in these steels.

However, due to experimental difficulties only very limited quantitative information is available for non-equilibrium segregation of boron in martensitic steels. Until recently, the detection of boron in steels had to rely on methods such as autoradiography or SIMS, which have limited spatial and chemical resolution. Only with the advent of the EELS [38], atom probe, and more recently atom probe tomography [40-43] we begin to get access to data with sufficient accuracy to generate data for modeling of the non-equilibrium segregation process.
Below, we present the first results of experimental investigations aiming at a detailed quantitative description of boron redistribution during normalizing of martensitic creep resistant steels.

Experimental methods

A forged 9Cr martensitic steel containing 108 ppm of boron (Fe–0.14C–0.084Si–0.33Mn–9.32Cr–1.49Mo–0.15Ni–1.25Co–0.2V–0.007Al–0.05Nb–0.029Cu–0.0197N–0.0108B, wt.%, bal. Fe) was selected for the current study. A cube sample of the steel with a side length of 15 mm was normalized at 1100°C for 1 h and cooled in air to provoke non-equilibrium segregation of the boron.

Thin-foil specimens for transmission electron microscopy were prepared by electropolishing with a solution of 10% perchloric acid in ethanol at the temperature of 240K and voltage of about 21-23 V using Struers “Tenupol-5” machine. TEM investigations were carried out on electropolished foils using a JEOL 3000F FEG TEM.

Electropolished specimens were used for site-specific preparation of APT tips. Site-specific APT samples containing PAGBs were prepared by FEI Helios NanoLab 600 using in-situ lift-out method and dual-beam FIB milling (Fig. 3). PAGBs were identified by ion tunneling technique in FIB. The PAGB was oriented at 90° to the tip axis (Fig. 3) in order to simplify its recognition at the final tip sharpening process and also to insure the presence of a PAGB in the fully prepared tip. To orient the PAGB at 90° the custom made sample holder with flip-out mechanism was used.

A transmission kikuchi diffraction detector (TKD) was applied in order to track the PAGB during final milling when displacing a boundary to the first 100 nm of the APT tip. TKD allows the mis-orientation of the PAGB to be measured.

APT analysis was performed using a local electrode atom probe Imago LEAP3000X HR. The measurements were carried out in laser mode at 65 K [44]. The acquired data were analyzed using IVAS 3.4.1 software.

Figure 3: Detailed method of site-specific sample preparation for APT: a) selecting a PAGB using ion tunneling; b) thin cut of 50 nm on PAGB for highlighting selected PAGB; c) lift-out lamella with perpendicular oriented PAGB; d) standard lift-out procedure with use of micromanipulator; e) attachment of sample to a preshaped needle; f) verification of PAGB within first 100 nm of final milled tip using TKD.

Results and discussions

APT
The final APT tip containing a perpendicular oriented PAGB with misorientation of 52° located about 50 nm from the top is shown in Fig. 3f. The reconstructed APT tip collected approximately $2.6 \times 10^6$ atoms representing the atom distribution maps of B, Cr, Fe, C, Co and Mo in a $50 \times 50 \times 140$ nm$^3$ analytical volume (Fig. 4). These maps indicate a conglomeration area in the vicinity of the PAGB, which is rich in B, Cr, C and Mo, and with strong depletion of Fe and Co. The interface between the atom conglomeration and the prior austenite grains is completely even on one side, whereas the other side is roundish. The average thickness of atom conglomeration area was found to be 14 nm.

![APT image of CrB boride at the PAGB in as-quenched at 1100°C martensitic steel containing 108 ppm of boron. Distribution of B, Cr, Fe, C, Co, Mo atoms.](image)

1-D concentration profiles were taken across the conglomeration area in three places, figure 5. The composition profile in the thick part (Fig. 5) shows a peak with high concentration of B and Cr atoms. The boron concentration value was 33 at. % which is three orders of magnitude higher than the nominal value of 0.06 at.% (108 wt ppm). Also Mo, V and C were strongly enriched in this area whereas Fe, Co and Si were depleted. The high Cr and B levels, in amount of 33 at.% and 36 at.%, respectively, together with Fe and Mo in amount of 20 at.% and 6 at.%, respectively, indicate a M$_2$B-type particle, where M is Cr, Fe and Mo – substitutional atoms.

M$_2$B borides usually precipitate as coarse particle (20-100 μm) during solidification. However, fine M$_2$X borides were found in austenitic steels containing 20 to 40 ppm of B using APT and energy filtered transmission electron microscopy.
The chemical composition and stoichiometry of the detected boride in comparison with M\textsubscript{B}2-type borides found in \cite{33} are given in table 2. The thickness of observed boride is 14 nm while most of the borides investigated in \cite{45} are 15–30 nm thick and 80–300 nm long. The average size of borides found in \cite{33} increased from 50 to 700 nm with decreasing cooling rate and with increasing holding temperature, showing a high sensitivity of boride growth to the heat treatment parameters.

![Figure 5: 1-D concentration profiles across precipitate area in a boron added martensitic steel. The thick, thin and thinnest parts marked by red lines on APT tip, respectively.](image)

The amount of detected B and Cr atoms in the thin part of the conglomeration decreases down to 20 and 30\%, respectively, while Fe increases up to the level of 40\%. This tendency continues with moving 1-D profiles to the thinnest part (red lines in the figure 5). In the thinnest part the compositions of all elements except for B are homogeneously distributed across the analyzed area. Boron atoms are found to be segregated in amount of 2 at.\% with thickness of 10 nm, corresponding to 33 times the overall boron concentration in the steel. The observed B concentration in the thinnest part of analyzed area indicates non-equilibrium segregation of B on the PAGB. The boron level corresponds to published results from other low-alloy martensitic steels \cite{40-43, 46}. The mechanism of boride nucleation on PAGBs can be explained by abundance of boron atoms segregated to the PAGBs by non-equilibrium process during quenching.

<table>
<thead>
<tr>
<th></th>
<th>B</th>
<th>Cr</th>
<th>Fe</th>
<th>Mo</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>M\textsubscript{1.7}(B,C)</td>
<td>35</td>
<td>29</td>
<td>13</td>
<td>21</td>
<td>2</td>
</tr>
<tr>
<td>M\textsubscript{1.8}(B,C)</td>
<td>26</td>
<td>36</td>
<td>10</td>
<td>27</td>
<td>2</td>
</tr>
<tr>
<td>present work</td>
<td>33</td>
<td>38</td>
<td>20</td>
<td>6</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 2. Composition of PAGB borides. Atom-probe analysis (at.%).

It was predicted \cite{45} by thermodynamic software MT-DATA that at GB concentration of boron in amount of 0.0027 wt.\%, M\textsubscript{B}2 borides were unstable. The nucleation rate of borides at lower GB boron concentration was sensitive to the grain boundary interfacial energy, which could lead to the formation of borides on preferential PAGBs. In contrast to that, at high GB boron concentration borides were predicted to be formed on PAGBs homogeneously and independently on the interfacial energy.

For verification of this theory, additional TEM investigations were performed in the present material.

**TEM**
TEM inspections of about five PAGBs in the present martensitic steel in as-quenched condition showed no presence of borides on the investigated boundaries (figure 6). Meanwhile, Sourmail \[45\] reported that CrB precipitates were detected only on a few PAGBs. In addition, the precipitate density on different PAGBs was not identical. It can also be explained by different misorientations of PAGBs and, therefore, different PAGBs widths, containing different amounts of boron concentrations. It was shown in \[47\] that the degree of segregation strongly depends on the grain boundary misorientation. Comprehensive analysis of large number of PAGBs has to be performed for establishing a systematic model of formation of borides.

Figure 6: TEM micrographs of typical borides free PAGBs in martensitic steel containing 108 ppm of boron after quenching.

Conclusion

Recently developed advanced techniques such as APT, EELS have provided quantitative analysis of boron for determination of its behavior and role in boron containing alloys. Present study reveals the presence of plate-shaped CrB borides with thickness of 14 nm in martensitic steel containing 108 ppm of boron. According to the published results such borides have not been found previously in martensitic steels. Quantitative analyses of CrB precipitate indicates following chemical composition: 33 at.% B, 36 at.% Cr, 20 at.% Fe, 6 at.% Mo, 5 at.% V, 2 at.% C.

Obtained results support that boron segregates during quenching from austenite and appears on PAGBs by non-equilibrium mechanism. CrB borides nucleate on some PAGBs consuming non-equilibrium segregated atoms of boron, while most of PAGBs are found to be boride free. Further investigations of boron is required for complete understanding its positive effect on creep strength of boron added martensitic steels.

Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>PAGBs</td>
<td>Prior austenite grain boundaries</td>
</tr>
<tr>
<td>APT</td>
<td>Atom probe tomography</td>
</tr>
<tr>
<td>EELS</td>
<td>Electron energy loss spectroscopy</td>
</tr>
<tr>
<td>NanoSIMS</td>
<td>Nano scale secondary ion mass spectrometry</td>
</tr>
<tr>
<td>HT</td>
<td>Heat treatment</td>
</tr>
<tr>
<td>TKD</td>
<td>Transmission kikuchi diffraction</td>
</tr>
<tr>
<td>EFTEM</td>
<td>Energy filtered transmission electron microscopy</td>
</tr>
<tr>
<td>FIB</td>
<td>Focus ion beam</td>
</tr>
</tbody>
</table>

References


[18] Strocchi P. M.; Melandri B.A.; Tamba A.: On the nature of boron solid solution in a-Iron; Centro SperimentaleMetalurgico (1967)
[41] Seol, J. B.; Lim, N. S.; Lee, B. H.; Renaud, L.; Park, C. G.: Atom probe tomography and nano secondary ion mass spectroscopy investigation of the segregation of boron at austenite grain boundaries in 0.5 wt.% carbon steels; Met. Mater. Int., 17, 413–416 (2011)
Appendix B

Manual for site-specific sample preparation
Appendix A

Site-specific sample preparation for APT (using Helios NanoLab 600)

Irina Fedorova
Flemming Bjerg Grømosen

Preparation for a microscope session, check-list:
1. sewing needles with smallest size (Fig. 1a) fresh electropolised with 10 pct perchloric acid in ethanol;
2. electropolished with 10 pct perchloric acid in glacial acetic acid by Tenupoll 5 thin foils attached to the standard SEM holder (Fig. 1b);
3. custom-made needle holder with flip-out mechanism (Fig. 1c-d).
Fig. 1 – Electropolished needles (a), specimens (electropolished thin foils) (b), needle holder: in horizontal position (c), in vertical position (d).

**IMPORTANT!!** Gold coating on polished needles is necessary for preventing them against corrosion (Fig. 2).

![Image of coating machine](image-url)

**Fig. 2** – Quorum Q 150T ES coating machine for gold coating of needles.

**Inserting a sample**

1 lab manager → log in → start operating
2 hit VENT → open the blue tap over the microscope (waiting time is apx. 10 mins)
3 open the chamber (Fig. 3a) and set up right configuration using the round-shaped holder (Fig. 3b)
4 fix your sample on the top (Fig. 3b), adjust the height
5 close the chamber, hit PUMP and gently push the chamber door a bit for the first 5 sec.
6 wait for a good vacuum, when ▲ becomes green ▲
7 hit WAKE UP, and then BEAM ON
Fig. 3 – A typical chamber in Helios SEM machine (a), a typical sample setup (b).

**General alignments**

1 in EB (10kV): find your sample (using different mags), adjust focus, stigmator.
2 link the sample, adjust working distance Z=4.15, refocus+link
3 find a feature, move it to the center (double click)
4 CTRL+I (or T=52°), track the feature, replace it in the center using the bottom right window by scroll wheel.
5 in IB (26 pA; 30kV): adjust a feature by SHIFT+left mouse button

**Tunneling**

1 set up T=52°; 30kV; 0,44 nA
2 hit ▶ to start scanning, when the structure appears, stop by 
3 select a PAGB (Fig. 4a), rotate it to the vertical position (stage-vertical) (Fig. 4b)
Fig. 4 – Ion tunneling: Identification and selection a GB (a), rotation a selected GB to the vertical position (b).

4 mark a boundary by slight cut (Si dep, 1 sec, Z=0.05 μm, 0.5 nA) (Fig.5)

Fig. 5 – A marked GB.

**Cutting**

**First cut:**
1 set up T=22°; 2.5 nA; Si dep; Z=3 μm; y=2 μm
2 check both EB and IB windows, readjust (if necessary)
3 select square pattern
4 hit SNAPSHOT
5 hit ➤ to start (Fig. 6)

Fig. 6 – A typical image of FIB first cut.

**Second cut:**

1 rotate the sample for 180° (select ΔR=180°);  
2 check the settings (T=22°; 2.5 nA; Si dep; Z=3 μm; y=2 μm)
3 place the pattern above the first cut by 2 μm (Fig. 7a)
4 check both EB and IB windows, readjust (if necessary)
5 hit SNAPSHOT
6 hit ➤ to start (Fig. 7b)

Fig. 7 – A typical image of FIB second cut.
Third cut:
1 tilt the sample to $T=52^\circ$
2 check the settings ($T=52^\circ$; 2.5 nA; Si dep; $Z=3 \, \mu m$; $x=2 \, \mu m$)
3 hit SNAPSHOT
4 hit \( \rightarrow \) to start (Fig. 8)

Fig. 8 – A typical image of FIB third cut.

First clean-up cut:
1 tilt the sample to $T=22^\circ$
2 select “cleaning cross section” pattern; advanced mode \( \rightarrow \) rotation by $180^\circ$ (thick line must be on the bottom part of the pattern)
3 set up $30kV$; 0.44 nA; $Z=1 \, \mu m$
4 place the pattern on the upper cut
5 hit SNAPSHOT
6 hit \( \rightarrow \) to start (Fig. 9a)

Second clean-up cut:
1 rotate the sample for $180^\circ$ (select $\Delta R=180^\circ$); \( \square \) Compucentric rotation
2 check the settings ($T=22^\circ$; 0.44 nA; Si dep; $Z=1 \, \mu m$)
3 select “cleaning cross section” pattern; advanced mode → rotation by 180° (thick line must be on the bottom part of the pattern)
4 place the pattern on the upper cut (Fig. 9b)
5 check both EB and IB windows, readjust (if necessary)
5 hit SNAPSHOT
6 hit ↘ to start (Fig. 9b)

![Fig. 9 – An image taken after first clean cut (a), second clean cut (b).](image)

**Inserting omniprobe**

1 set up T=0°, select view current
2 stage Z=original position + 2 mm (to be in safe zone), insert omniprobe, check the position, adjust if necessary, retract omniprobe
3 stage back to the original position
4 insert GIS pt dep ≠ heat up GIS by double-click on “cold”
5 insert omniprobe ≠
6 place omniprobe near by the edge of the sample (Fig. 10a) using both EB and IB windows, buttons on the panel and decreasing constantly mag.
7 weld micro-manipulator to the end of the sample using both pt dep and EB (Fig. 10b). It must be done twice: for small pattern area – 26pA, $Z = 0.5 \ \mu m$; for bigger one-90pA, $Z = 0.2 \ \mu m$

8 cut the last side of the sample ($T = 0^\circ$; 0.28 nA; Si dep; $Z = 3 \ \mu m, x = 2 \mu m$) (Fig. 10c)

IMPORTANT!!! Do not use double click for replacing your sample while it is attached on both sides, it will destroy the sample. Use SHIFT+left mouse button.

9 lift the sample out slowly in zigzag way (Fig. 10d)
10 move omniprobe to the pack position; retract omniprobe out
11 GIS out
12 hit VENT
Fig. 10 – Lift-out procedure: Omniprobe placed near be the sample (a), omniprobe attached to the edge of the sample (b), sample free of the bulk (c), lift-out omniprobe with attached sample (d).

**Placing a lifted-out sample to the needle**

1 fix an electropolished needle to the needle holder in a horizontal position
2 insert to the chamber
3 hit PUMP
4 find the needle, adjust focus, stigmator.
5 link to the needle, adjust working distance Z=4.15, refocus+link
6 find a feature, move it to the center (double click)
7 CTRL+I (or T=52°), track the feature, replace it in the center using the bottom right window by scroll wheel.
8 in IB (26 pA; 30kV): adjust a feature by SHIFT+left mouse button
9 insert GIS □
10 insert OMNIPROBE □
11 place the sample close to the needle using both EB and IB windows, buttons on the panel and decreasing constantly mag (Fig. 11).

Fig. 11 – Placing a sample to the needle.
12 weld the sample to the needle using both EB and IB (90 pA, 2 times)

**IMPORTANT:** use only SHIFT+left mouse button for replacing (if necessary)

13 cut of the omniprobe (0.28 nA) (Fig. 12)
14 retract omniprobe
15 remove GIS
16 hit VENT

![Fig. 12 – A sample free of the omniprobe](image)

**Depositing**

1 fix the needle in the vertical position (Fig. 13a)
2 down the stage
3 hit PUMP
4 make general adjustments
5 insert GIS → PT dep using EB and IB (90 pA it must be done in the right corner (Fig. 13b)) → retract GIS
6 rotate needle R=90°
7 repeat item 5  
8 rotate needle R=90°  
9 repeat item 5  
10 stage Z=original position + 2 mm (to be in the safe zone)

Fig. 13 – A needle in the vertical position ready for Pt dep.

Milling/Sharpening

1 select a circle pattern  
2 select a proper outer and inner diameter sizes and beam current  
3 decrease diameters and currents step-by-step (Fig. 14)  
4 when you finish, perform a cleaning milling at 2kV, 27pA and with inner d = 0 μm  
**IMPORTANT!!!** Track a GB using TKD (Fig.15)
Fig 14 – Final milling.

Fig. 15 – Checking the misorientation of PAGB by TKD.

**Cleaning of manipulator**

1 clean manipulator on both sides
2 rotate manipulator manually by 90°
3 repeat item 1
4 rotate manipulator back

IMPORTANT!!! Do not leave unclean micromanipulator (Fig. 16)!
Fig. 16 – An example of unclean manipulator.
Creep resistant martensitic 9-12% Cr steels are preferred materials for turbines, pipes and castings of fossil fuels because of their excellent combination of high creep strength, corrosion resistance and relatively low cost. Efforts are ongoing to increase steam temperatures to 650°C by improving the creep strength and corrosion resistance of the martensitic steels. Corrosion resistance is achieved by increasing the Cr content up to 11-12%. However, so far the alloy concepts for martensitic 11-12%Cr steels have failed, since they relied on precipitation strengthening from fine MX ((V,Nb)(C,N)) carbonitrides, which transform into coarse Z-phase (Cr(V,Nb)N) nitrides causing a loss of precipitation strengthening and creep strength breakdown. In the present Phd project a promising alloying concept, which combine reduced nitrogen and added boron to provide microstructure stability of 9-12% Cr martensitic creep resistant steels is investigated. The aim of the research is to improve the understanding of strengthening mechanisms in low nitrogen creep-resistant steels. Investigations were made in two directions: microstructure characterization of new experimental 11% Cr martensitic steels and study of boron behavior in various 9-10%Cr martensitic steels.