Toward first-principles understanding of carbonitride precipitation in steels

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The cover picture shows the induced charge density in the (110)-plane for an interstitial (left) and a substitutional (right) boron atom in bcc iron. Red and blue correspond to charge accumulation and depleation respectively while green represents the undisturbed charge density.

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ABSTRACT

The most important and widely used group of metallic alloys is steels, which are alloys of the element iron together with carbon and usually other elements such as B, N, V, Nb and Cr. The strength in these alloys is closely connected to the distribution of point defects, precipitates and grain boundaries which effectively act as obstacles for dislocation migration. In the present thesis we aim to obtain a fundamental understanding of the precipitation of transition metal carbonitrides in steels.

In particular, we investigate the effect of boron diffusion on the coarsening rate of $\text{M}_{23}(\text{C,B})_6$ precipitates ($\text{M} = \text{transition metal}$) using density functional theory (DFT) calculations. The results show that boron predominantly enters as a substitutional solid solution in the iron matrix at low temperatures. At elevated temperatures the interstitial population can however not be neglected which leads to that boron diffusion under equilibrium conditions will be governed by the interstitial mechanism. Further, the corresponding diffusion rate is shown to be too fast in order to explain the coarsening rate of $\text{M}_{23}(\text{C,B})_6$ and it’s concluded that other possible mechanisms must be explored.

In addition, the energetics for semicoherent interfaces between the iron matrix and nacl structured MX precipitates ($X = C, N$) are studied using DFT in combination with a Peierls-Nabarro model. The electronic structure at the interface is characterized by covalent Fe(3d)-X(2p) and metallic Fe(3d)-M(d) bonds, where the strength of the metallic interaction is connected to the relative position of the M d-band and Fe d-band centers. In addition, it is shown that the elastic energy contained in the dislocation network, due to the lattice misfit at the interface, gives a significant contribution to the interface energy.

**Keywords:** Steels, Coarsening, Precipitates, Electronic structure, Interfaces, Density functional theory, Diffusion, Dislocation network, Peierls-Nabarro model, Misfit
LIST OF PUBLICATIONS

This thesis consists of an introductory text and the following papers:

I  **Nature of boron solution and diffusion in α-iron**  
   D. H. R. Fors and G. Wahnström  

II  **Interface energy trends for semicoherent Fe(001)/MX(001) systems using ab initio calculations**  
   D. H. R. Fors and G. Wahnström  
   (in manuscript)
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Chapter 1

Introduction

The steel industry has for centuries been a prominent factor for the infrastructure development which had led to that contemporary steels are by far the most used metallic alloys. The cheap manufacture process and the possibility to fine-tune the physical properties have made steels to an adequate material choice in both everyday life and industry where the alloys for example are used in knives, cars, pipes and storage tanks. The steel alloys can in general be very advanced and obtaining a basic understanding of the underlying processes which determine the material properties can constitute a major challenge.

In the present thesis the focus is directed on 9-12%Cr steels, which are a class of steel alloys that due to the high chromium content have very good oxidation resistance and sound creep strength at elevated temperatures (\(\sim 600^\circ C\)) [1, 2]. In particular, we concentrate on the precipitation process of transition metal carbides and nitrides in the alloy by using atomistic methods. The presence and time evolution of these carbonitrides have a governing role for the characteristic properties of the material. The project is a part of a larger collaboration between Chalmers University of Technology, The Royal Institute of Technology, The Technical University of Denmark and the companies Siemens and Sandvik; where expertise in creep modeling, thermodynamical modeling and experimental measurements are combined with the aim to understand the creep behavior of 9-12%Cr steel alloys. This is motivated by the usage of 9-12%Cr steels as a suitable material for thick section boiler components, turbine rotors, turbine vaults and steamlines in fossil power generating plants [1, 2].

The use of fossil power plants represents an important part in the global production of electrical power. Fossil fired combustion is utilized to convert water into superheated steam which drives turbines connected to electrical generators. The constant goal for these facilities is to increase the process efficiency and hence through lowered fuel consumptions achieve both a more cost-effective operation as well as reduced carbon dioxide emission. The operation efficiency can in theory be improved by raising the service temperature and/or the pressure. In practice this can however only be realized if there are materials with the ability to endure the higher temperatures and pressures during the entire lifetime of the plant (\(\sim 2 \cdot 10^5\) hours) without failing. The 9-12%Cr steel alloys have the suitable properties for these
conditions to reasonable manufacture costs and are today used in full production in power plants where the steam temperatures range up to 625°C [1]. Reaching higher temperatures would require an increased chromium content in order to obtain a sufficient oxidation resistance. This has however given rise to unforeseen material instabilities that lead to breakdowns in the long-term creep strength which have detrimental consequences for the lifetime of the components [3, 4], see chapter 3. There is therefore at the present time an intense research to understand these instabilities in order to either improve the current alloys or develop new possible materials that allow for the higher steam temperatures.

The outline of this thesis is the following. Chapter 2 gives a brief presentation of the general properties and processes in a material with focus on precipitation theory while steel alloys are discussed in more detail in Chapter 3. This is followed by a description of the computational method used in Chapter 4. Chapter 5 and 6 serve as an extended introduction to Paper I and II respectively. The thesis concludes with an outlook in Chapter 7.
Chapter 2

Material properties and processes

2.1 Structure of materials

The physical properties of solids, such as strength, hardness and ductility, depend on the specific features occurring at multiple length scales ranging down from the atomic level up to the macroscopic level. The crystal structure, chemical composition, grain sizes, defects and topological arrangement of phases will together constitute the microstructure at the mesoscale (1-100 µm) from where the connection to the macroscopic behavior can be made. In general the different parts are not in equilibrium and the microstructure evolution becomes a complex mechanism where many different processes such as diffusion, dislocation or grain boundary movements and phase transformations occur and interact across several different time scales. One of the key elements to fundamental understanding in all contemporary material research is therefore to obtain information about the underlying structure of the materials.

Today there are several experimental techniques available to probe the microstructure for a material. Commonly used methods include the scanning electron microscopy (SEM), energy-dispersive X-ray spectrometry (EDX) and transmission electron microscopy (TEM). In SEM the specimen is bombarded with a electron beam and the secondary and backscattered electrons are collected. Together with EDX, where the emitted X-rays from the sample are analyzed, SEM provides a powerful way to gain information about the topography and composition of materials. The principle behind the TEM technique is very similar to SEM but in contrast the wavelengths are shorter and the specimen must be very thin, which allows for a higher resolution than the SEM. Using the diffraction patterns from the transmitted electrons it’s possible to determine the type of structure and lattice parameters.

2.2 Material processing

The main goal in material engineering is to be able to control the physical properties in order to improve desired characteristics and to tailor them for specific applications. In order to change the microstructure the material is typically put through a
series of different external processes, where heat treatment constitutes a significant element.

The heat treatment is a multistep process where the very first step consists of supersaturating alloying elements in the material matrix and increasing the temperature to form a solid solution. Once the additives have reach a desired uniform distribution, the material is quenched\(^1\) at a high cooling rate. The alloy then enters a tempering cycle at temperatures lower than the initial solutionizing temperature. During this stage the alloying elements will be able to diffuse through the matrix and due to the change in solubility they will segregate to possible nucleation sites, such as grain boundaries or dislocations. Precise manipulation of the temperature and tempering time allows the resulting microstructure to be controlled.

An alternative or addition to heat treatment is work hardening. By applying external stress fields dislocations are created through plastic deformation. The number of dislocations formed will be large and they will in a way constitute an entangled network where the induced strain fields within the matrix will restrict any dislocation movements. This will effectively increase the required stress to deform the material. Caution should however be made since too aggressive work hardening can have the opposite effect and make the material brittle.

2.3 Defects and deformation

The presence and distribution of defects, such as point defects, dislocations, interfaces and secondary phases are crucial elements which determine the strength of a material and how it responds to applied stresses. In 1934 Taylor, Orowan and Polanyi independently discovered how crystals can flow by the concept of dislocations. The dislocations are line defects which allows for plastic deformation under stress. Only a few atomic bond need to be rearranged at the same time at the slip plane in order to create the movement. The dislocation mobility divides materials into two separate categories: ductile where the dislocations are able to move and brittle where the movements is heavily restricted. The latter instead deforms through crack propagation. The distinction between ductile and brittle is however not straightforward and will depend on the capability of the material to blunt cracks by emitting dislocations [5]. Covalent and ionic compounds generally tend to be brittle due to the directional bonds while many metals are ductile. The grain structure also plays a significant role where the grain boundaries limit the mean free path for the dislocations. In a fine grained material however the possibility for grain boundaries sliding increases and the segregation of additives can cause embrittlement at interfaces which make the material prone to crack [6]. A known example involves boron and sulfur which cause intergranular embrittlement in iron [7].

Creep is the technical term for plastic deformation under load for long time periods. The material resistance to creep and its evolution is of utter industrial impor-

\(^1\)During quenching the specimen is rapidly cooled down in order to prevent low-temperature processes such as phase transformations from occurring.
tance since it will determine the lifetime of the components in a given application. If the creep process is allowed to continue long enough the material will eventually fail. This doesn’t necessary means that it will rupture but rather refers to that it is rendered useless, which for instance happens when turbine rotors are elongated in such a way that they hit the turbine wall.

The plastic deformation goes through several different stages [8]. At low shear stress the deformation process will involve diffusional flows in order to compensate for the internal stress fields. The material will flow by the vacancies migration along grain boundaries at low temperatures or by lattice diffusion at higher temperatures. By raising the stress further dislocations and grain boundary sliding are activated and the material enters a phase with steady state deformation. Ultimately the material will fracture at sufficiently high stress levels, due to crack formation.

2.4 Precipitation of secondary phases

The heat treatment will change the microstructure either by deformation followed by recovery and recrystallization; or by various phase transformations. The latter is divided into polymorphous transformations where the matrix structure itself changes and precipitate transformations where alloying elements will fall out from the matrix and form a secondary phase. The main method to modify the microstructure is through precipitate transformations and we therefore direct our attention to this process. The precipitates are essential for the creep properties as they act as hardening objects for the material by a mechanism denoted as dispersion strengthening. The precipitates will constitute obstacles for the dislocations, which must cut through, bow around or climb out of their slip plane by the use of vacancies, in order to avoid the secondary phases and continue their movements [9]. All these mechanism require energy and the mobility barrier will effectively be increased.

Now consider a phase $\alpha$ where solute atoms, denoted by B, have been dissolved. The phase diagram for this system is shown in Fig. 2.1. At sufficiently high temperature the matrix will be able to contain the concentration $c_0$ of B in solid solution. However, when the temperature is lowered the $\alpha$-phase will become unstable and it will be more energy favorable to create a mixture of $\alpha$-phase with concentration $c\alpha$ together with a secondary phase $\beta$ with concentration $c\beta$. The precipitation can occur through two different types of phase transformation. The first type occurs when there is a distinct composition and structural difference between the $\alpha$ and $\beta$ phases. The nucleus of the secondary phase will then be confined to a small part of the matrix and a well-defined interface will be established between the two phases. The second type occurs when for instance the $\alpha$-phase has a metastable equilibrium at a higher concentration. Composition fluctuations in the alloy can then lead to a continuous decomposition into a mixture of the stable and metastable phases. The transformation, referred to as spinodal decomposition, can be delocalized in space and there will not emerge a well-defined interface between the two phases. In this work we are only concerned with the first type of transformation. The formation and evolution of the precipitates are in this case divided into three stages; nucleation, growth
and coarsening. The two first stages occur already during the tempering cycle while coarsening will occur during operation service.

### 2.4.1 Nucleation

Nucleation is the initial step in the phase transformation where the core of the new phase is created. The fundamental element in nucleation theory is that, when the new phase forms, an interface to the parent phase will be produced. The driving force for the process is the free energy difference between the two phases which for the nucleation of phase $\beta$ from phase $\alpha$ can be expressed as

$$
\Delta G = -V_\beta \Delta G_{\alpha \beta} + A \gamma,
$$

(2.1)

where $V_\beta$ is the volume of phase $\beta$, $\Delta G_{\alpha \beta}$ the free energy difference per volume between the $\alpha$ and $\beta$ phase, $A$ the interface area and $\gamma$ the interface energy. The volume of the new phase will in general not occupy exactly the same volume as the parent phase which gives rise to possible matrix distortions. The strain energy per volume $\Delta G_E$ required to incorporate the $\beta$ phase into the $\alpha$ phase must then also be included in the free energy difference according to

$$
\Delta G = -V_\beta \left( \Delta G_{\alpha \beta} - \Delta G_E \right) + A \gamma.
$$

(2.2)

In nucleation modeling the required parameters are often taken from the corresponding macroscopic values. The use of these values is however very questionable since it’s very unlikely that a small number of atoms will represent the same macroscopic properties as when the system size is large. Obtaining the true atomic values is then important in order to accurately describe the nucleation.
The difference in free energy for small radii will be dominated by the increase in surface area and therefore be proportional to the square of the particle radius \( R \). At larger radii the volume term dominates and the free energy difference decreases proportional to the cube of the radius. The two competing terms lead to a nucleation barrier \( \Delta G_{\text{crit}} \) which the new phase must overcome in order to create a nucleus, see figure 2.2. For a spherical nucleus the nucleation barrier and the corresponding critical radius \( R_{\text{crit}} \) are given by

\[
\Delta G_{\text{crit}} = \frac{16}{3} \frac{\pi \gamma^3}{(\Delta G_{\alpha\beta} - \Delta G_E)^2},
\]

\[
R_{\text{crit}} = \frac{2 \gamma}{\Delta G_{\alpha\beta} - \Delta G_E}.
\]

The result shows that the nucleation barrier will strongly depend on the interface energy and it is thus very important in nucleation modeling. The sensitivity to the interface energy lead to specific orientation-relationships between the matrix and the precipitate to allow for good atomic fit, which will minimize the interface energy. The mutual structure relationship in different directions will in turn determine the equilibrium shape of the second phase. The impact of the interface energy also gives that in some cases the phase that forms will not be the equilibrium structure, but instead a metastable phase with good atomic fit and low interface energy.
With \( N \) possible nucleation sites per unit volume the concentration of critical-sized nuclei can be expressed as

\[
n_{\text{crit}} = N \exp \left( -\frac{\Delta G_{\text{crit}}}{k_B T} \right).
\]  

(2.5)

The steady state nucleation rate \( I \) will then be given by the product between the concentration of critical-sized nuclei and the rate per second with which each nucleus can become supercritical, i.e.

\[
I = n_{\text{crit}} \omega \exp \left( -\frac{\Delta G_m}{k_B T} \right),
\]  

(2.6)

where \( \Delta G_m \) is the activation barrier for atomic migration across the interface while \( \omega \) is a factor which depends on the atomic vibration frequency and the interface area. In practice this simple expression must then also be corrected for the loss of critical-sized nuclei and the time it takes to reach a steady state reaction.

The above expressions hold for homogeneous nucleation, that is when there is no site preference and the nucleus formations occur randomly in the matrix. The nucleation barrier can however be effectively lowered by the presence of defects in the parent phase, so called heterogeneous nucleation. By nucleation at or in the vicinity of dislocations, grain boundaries or stacking faults a part of the existing defect will be destroyed and the accompanied energy release will lead to a reduction of the nucleation barrier and an increase in the nucleation rate. However, whereas the number of available nucleation sites \( N \) in homogeneous nucleation is all atom sites, heterogeneous nucleation provides only a significantly reduced number of sites. This will counteract the barrier reduction by decreasing the nucleation rate. The nucleation in solids however often tends to be dominated by heterogeneous nucleation.

### 2.4.2 Growth

The subsequent stage after the nucleation process is called growth. The nuclei will grow larger by depleting alloying elements from the matrix and accommodate them in the precipitates. Depending on the active mechanism the growth can be either diffusion or interface controlled. In the former the transfer mechanism at the interface is so fast that the mass transport to the interface by diffusion will be the bottleneck. In contrast for the interface controlled growth the diffusion rates are sufficiently high so that the interface transfer mechanism will become the rate limiting process.

When the interface reaction is fast a local equilibrium will emerge at the boundary and the interface concentration just outside the particle will be given by \( c_i = c_\alpha \), cf. Fig. 2.3. The concentration far from the particles \( c_\infty \) is initially given by \( c_\infty = c_0 \) and will then slowly decrease until the equilibrium concentration in the \( \alpha \)-phase is reached, i.e. \( c_\infty = c_\alpha \). If there now is a low solute saturation while the solute atoms diffuse across the depleted region the solute distribution and particle size can be regarded as approximately constant. It is then possible to solve the Laplace equation to obtain the steady state concentration profile as

\[
c(r) = c_\infty - \frac{R}{r} (c_\infty - c_\alpha).
\]  

(2.7)
2.4 Precipitation of secondary phases

Figure 2.3: The concentration of the solute atoms across the $\beta/\alpha$ interface. The depletion creates a concentration gradient outside the solute-rich $\beta$ precipitate.

The corresponding flux of solute atoms per second across the surface of a sphere with radius $r > R$ is given by

$$J = -\frac{4\pi D}{V_a} r^2 \frac{dc}{dr} = -\frac{4\pi D}{V_a} R (c_\infty - c_\alpha), \quad (2.8)$$

where $D$ is the diffusion coefficient and $V_a$ is the volume per atom. Due to the inward flux of atoms the particle will grow according to

$$\frac{dR}{dt} = \frac{D}{R} (c_\infty - c_\alpha), \quad (2.9)$$

or

$$R(t) = At^{1/2}, \quad (2.10)$$

where

$$A = (2D (c_\infty - c_\alpha))^{1/2}. \quad (2.11)$$

We have assumed that $R(t = 0) = 0$, $c_\beta \approx 1$ and $c_\alpha \ll c_\beta$. From the expression one finds that the driving force will depend on the diffusion rate as well as the difference between the instantaneous concentration in the $\alpha$-phase $c_\infty$ and the equilibrium $\alpha$-phase concentration. As the concentration in the matrix approaches the equilibrium value the growth rate will therefore gradually decrease. With time the diffusion fields will also start to overlap and the precipitates will start to compete with each other for the constituting elements.
The above model assumes a fast interface mechanism. This criterion may however not always be fulfilled. The probability for the solute atoms to move across the interface and find an available site will depend on the presence or absence of good atomic fit across the interface. For incoherent interfaces the activation barrier is expected to be in the order of grain boundary diffusion and there is no difficulty for the atoms to accommodate a site in either phase after crossing the interface. In contrast growth of coherent precipitates, where the lattice structure with respect to the matrix is different, will experience a significant barrier due to the difficulty to find an energy favorable site after the crossing. The atoms will then instead be added on ledges or steps by diffusion or dislocation slide. At coherent interfaces with the same structure there is however no problem adding atoms onto the growing phases.

2.4.3 Coarsening

The final stage in formation of the secondary phases is coarsening also known as Ostwald ripening. The process refers to the course of events following when the concentration in the parent phase has reached the equilibrium value and the precipitates have reached their equilibrium volume fraction. However, there is still a driving force in the system since the free energy can be lowered further by reducing the interface area.

The precipitate curvature will generate an increased pressure with respect to the surrounding matrix, which for a spherical precipitate will be inversely proportional to the radius \([11]\). The increase in Gibbs free energy in turn shift the chemical potentials close to the interface. The corresponding concentration change for a dilute distribution of B atoms in the \(\alpha\)-phase can be expressed as

\[
c_R - c_\alpha = \frac{2\gamma V_a c_\alpha}{R k_B T}, \tag{2.12}
\]

where \(c_R\) is the concentration just outside a particle with radius \(R\). The concentration of element B outside each particle will thus depend on the radius size. This leads to a concentration difference between two particles according to

\[
c_{R_2} - c_{R_1} = 2\gamma \left(\frac{1}{R_2} - \frac{1}{R_1}\right) \frac{V_a c_\alpha}{k_B T}. \tag{2.13}
\]

Now consider a particle distribution with the average radius \(\bar{R}\). Within the steady state approximation, cf. Eq. 2.9, we can obtain the growth rate of a particle having the radius \(R\) as

\[
\frac{dR}{dt} = D \frac{R}{R} 2\gamma \left(\frac{1}{\bar{R}} - \frac{1}{R}\right) \frac{V_a c_\alpha}{k_B T}. \tag{2.14}
\]

This implies that precipitates larger than \(\bar{R}\) will growth while smaller ones will dissolve, cf. Fig. 2.4. During coarsening the average radius will gradually increase until a steady state distribution is reached. The time evolution of the particle distribution
2.4 Precipitation of secondary phases

Figure 2.4: Schematic figure over the coarsening process. The large particles will grow on the expense of the smaller ones.

have been derived by Lifshitz, Slyozov and Wagner [12, 13] and the corresponding coarsening rate is given by

\[ \bar{R}^3 - \bar{R}_0^3 = Kt, \]  \hspace{1cm} (2.15)

where \( \bar{R}_0 \) is the initial average particle size and the coarsening constant \( K \) is given by

\[ K = \frac{8}{9} \frac{D \gamma V_a c_\alpha}{k_B T}. \]  \hspace{1cm} (2.16)

It is worth to note that the volume fractions and average particle sizes play an essential role in coarsening modeling. This information can be obtained by experimental measurements by using Energy-Filtered Transmission Electron Microscope (EFTEM) based on the information from the Electron Energy Loss Spectra (EELS). It’s then possible to get accurate particle size measurements down to a few nm. For mean particle sizes larger than 100 nm EFTEM however becomes inefficient and SEM are often used instead [2].
Chapter 3

Steels

The most important and widely used group of metallic alloys is steels. In contrast to pure iron, which is extremely weak, steel alloys display yield stresses within the large range 200 MN/m$^2$ - 5500 MN/m$^2$ [14]. The different microstructures can be very complex but the key element connecting them all is the addition of carbon. The carbon influence in these alloys can commonly be direct connected to the behavior of plain iron-carbon steels. Adding only a small amount of carbon (0.1-0.2 wt%) to pure iron is sufficient in order to significantly raise the strength by interstitial solid solution strengthening. The strain fields from the interstitial carbon atoms in the solid solution will interact with the strain fields from the dislocations which results in a reduction of the total strain energy. The dislocations are therefore effectively pin downed which will decrease there mobility and thus increase the yield strength.

The principle phase diagram for the plain iron-carbon steel at higher carbon concentrations is shown in Fig. 3.1. The phase structure is determined by the difference in carbon solubility between ferrite ($\alpha$-iron) and austenite ($\gamma$-iron). The carbon solubility is significantly higher in austenite ($\sim$ 0.8-2.0 wt%) than in ferrite ($\sim$ 0.0001-0.02 wt%) which leads to rejection of carbon from the matrix during the austenite to ferrite phase transformation. The excess carbon will instead precipitate into iron carbide Fe$_3$C (cementite). Quenching under slow cooling rates across the eutectoid temperature 723°C will produce pearlite which is a lamellar mixture of ferrite and cementite. The fine pearlite structure can give a significant increase to the strength but has an adverse effect on the ductility and toughness since the ferrite/cementite interfaces provide easy crack formation sites. Quenching at higher cooling rates will result in metastable martensite where the carbon atoms remain in supersaturated solid solution in ferrite. The phase forms by a sudden shear transformation in austenite, which is not followed by any atomic diffusion, producing a tetragonal distorted ferrite structure. The shear transformation produces a high dislocation density and gives a very hard although brittle material. By tempering the material to some extent the internal stress fields are allowed to relax, which in turn increases the ductility. The martensitic steels are then ideal to use for example in cutting edges of knives or other kitchen supply [15].

A high fraction of the steels used in the industry has a plain iron-carbon structure where a small amount of alloying elements, such as Mn or Si, is added just for steel-
making purposes. An increased fraction of alloying elements will shift the relative stability between phases by either expanding the \( \gamma \)-field or contracting the \( \gamma \)-field while expanding the \( \alpha \)-field. The transformation temperatures for the ferrite and pearlite reaction are thereby shifted as well. The key with the alloying elements is often to slow down the ferrite and pearlite reactions so that these can be more readily avoided during the heat treatment. This will in turn allow for the formation of the stronger martensite structure. At significantly high concentration many elements, such as Cr, Mo, V, Ti or Nb, will form carbides that are more stable than cementite, which can reduce or even eliminate the pearlite phase. The remaining amount of alloying elements will typically contribute to the solid solution strengthening.
3.1 9-12%Cr steels

The 9-12%Cr steels are a class of materials with good oxidation resistance and sound creep strength. The steels are characterized by a fine martensite lath microstructure stabilized by $M_23C_6$ carbides ($M = \text{metal atom}$). The structure forms during the cooling process subsequent to the annealing treatment around 1050°C. In order to recover ductility the steels are then tempered in the range 680-780°C, where the exact choice of temperature depends on the specific application. During the tempering stage dislocations are annihilated while ferrite subgrains and carbonitrides will start to nucleate and grow. The final microstructure will have a high dislocation density and a relatively small subgrain sizedistribution [1, 2]. The lath structure for two steels currently under development, denoted by KB and KP, can be seen in Fig. 3.2 while the corresponding compositions are presented in Tab. 3.1.

The main deformation mechanism in the 9-12%Cr steels, under the relevant operation conditions, is the migration of boundaries and dislocations. The recovery of the lath structure during long-term creep leads to decreased creep strength and eventually to rupture. The detrimental evolution is however effectively retarded by the presence of precipitates, which pin down the boundaries and dislocations. The creep strength is therefore closely associated to the precipitate stability [2].

3.1.1 Composition

The main alloying elements in 9-12%Cr steels are Cr, Mo and W together with C and N. The Cr content, and also recently Si, is added in order to prevent the large oxidation problems which occur at the operating temperatures in question. The minimum amount to obtain sufficient oxidation resistance is typically around 9%Cr while increased temperature will require a higher content. The drawback is however that the austenite to ferrite transformation will gradually diminish with increased Cr

Figure 3.2: TEM bright field micrographs of a) steel KP after aging at 600°C for 54351 hours and b) steel KB after tempering at 740°C for 5 hours. Courtesy to A. Golpayegani and H.-O. Andrén [16].
Table 3.1: Chemical composition in the steels KB and KP. The data are obtained from [16].

<table>
<thead>
<tr>
<th>Element</th>
<th>KB [wt %]</th>
<th>KP [wt %]</th>
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</tbody>
</table>

amount until it eventually will disappear at approximately 12% [17]. To stabilize the austenite phase field within the 9-12% range Ni and Mn are therefore commonly added in addition to the already occurring γ-phase stabilizers C and N. The presence of Cr is also responsible for the formation of the primary M$_{23}$C$_6$ carbides.

The addition of Mo and W was previously believed to be beneficial for the long-term creep tests through substitutional solid solution hardening [3, 18]. The precipitation of the intermetallic Laves phase (Fe,Cr)$_2$(Mo,W)$_2$ during operation service [3, 19] will however lead to a depletion of Mo and W from the matrix, which would thereby counteract the hardening mechanism. Creep modeling of the Laves phase influence has also shown that the corresponding dispersion strengthening from the new large precipitates can’t compensate for the loss of the solid solution strengthening [20]. The beneficial influence of Mo and W instead comes from their incorporation in the M$_{23}$C$_6$ carbides which leads to a decrease in the coarsening rate due to the slow substitutional diffusion of Mo and W in the martensite matrix [2].

### 3.1.2 Boron addition

Boron additions around 20-100 ppm to 9-12%Cr steels can significantly improve the long-term creep strength, which is believed to be connected to an increased stability of the M$_{23}$C$_6$ carbides [21, 22]. Higher B content, as in the Japanese trial steel TAF [23], gives even higher creep strength but on the other hand makes welding and hot-forming difficult [22], which are two essential properties to preserve in the manufacture process. The experimental M$_{23}$C$_6$ particle size measurements in the steels KP and KB give the coarsening rates $1.05 \cdot 10^{-30}$ m$^3$/s and $0.60 \cdot 10^{-30}$ m$^3$/s respectively [22], cf. Fig. 3.3. The presence of boron will thus effectively decrease the coarsening rate by a factor 1.75. The exact mechanism for this reduction is however still not known [21, 22].
3.1 9-12%Cr steels

Figure 3.3: Mean radius of $M_{23}C_6$ precipitates in the steels KP and KB before and after long-term aging at 600°C. The experimental values (circles) are obtained from [22] and then fitted to the coarsening equation (Eq. 2.15).

During the cooling process subsequent to annealing boron atoms will segregate to the austenite grain boundaries, see Fig. 3.4. The process most probable occurs through a non-equilibrium mechanism where boron-vacancy complexes diffuse along vacancy gradients toward sinks at the boundaries [16, 24]. During the tempering stage $M_{23}C_6$ precipitates will primarily nucleate on the prior austenite grain boundaries or inside the grains on lath boundaries. They will then grow to the equilibrium volume fraction within a couple of minutes [25, 26]. Experimentally it has been shown that almost all boron atoms will be evenly incorporated into the $M_{23}C_6$ carbides and that only a extremely small amount (< 4 ppm) remains in the matrix [26]. At the grain boundaries there is thus a possibility for direct boron incorporation while boron atoms have to diffuse in order to reach the precipitates inside the grains. This leads to that the boron content in the $M_{23}C_6$ will depend on the distance from the grain boundaries.

3.1.3 V and Nb addition

The addition of V and Nb leads to the formation of a fine dispersion of $(V,Nb)(C,N)$ precipitates during the tempering stage. The particles are distributed both along the boundaries as well as within the grains. The precipitates are much more stable against coarsening than the $M_{23}C_6$ particles [2], mainly due to the lower matrix sol-
Figure 3.4: Left: Boron atoms segregate to prior austenite grain boundaries during cooling. Right: During tempering the boron atoms will diffuse both along grain boundaries and back into the grain at the same time as M$_{23}$C$_6$ carbides nucleate and grow.

ubility of V and Nb than Cr, which gives a crucial contribution to the creep strength by impeding dislocation migration.

Short-term tests (< 10 000 h) initially showed very promising creep properties for 9-12%Cr steels with V and Nb additions. However, the long-term creep tests (> 10 000 h) have revealed sudden changes in the microstructure stability leading to accelerated creep and an abrupt breakdown in the creep strength. The emerging microstructure instability has been connected to the formation of large coarse Z-phase Cr(V,Nb)N during operation [4]. The more stable Z-phase contains the same elements as the (V,Nb)N precipitates and will grow on their expense by dissolving a substantial number of particles. The dispersion strengthening from the (V,Nb)N precipitates will thus drastically decrease which results in a more rapid recovery of the lath structure. The formation of Z-phase will in addition be accelerated with increasing Cr content. This will in principle make it very hard to raise the service conditions since it requires a higher Cr content in order to obtain sufficient oxidation resistance. Understanding the Z-phase formation therefore constitutes a major focus in the contemporary development of 9-12%Cr steels.
Chapter 4

Computational methods

A central issue in condensed matter physics is to understand and to predict the physical properties of materials from first-principles, i.e. to start directly from the established laws of physics and not make any assumptions such as fitting a model to available experimental data. The ability to obtain such a fundamental understanding depends on how well the quantum mechanical behavior of the underlying interactions between electrons and nuclei can be described. In principle, a complete description for these many-body systems is given by the full Hamiltonian

\[ H = -\frac{1}{2} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_i \frac{Z_i}{|\mathbf{r}_i - \mathbf{R}_i|} \]

\[ - \frac{1}{2M_I} \sum_I \nabla_I^2 + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \]  (4.1)

where the electrons are denoted by lower case subscripts and the nuclei, with charge \( Z_I \) and mass \( M_I \), are denoted with upper case subscripts. Further \( \mathbf{r}_i, \mathbf{R}_i \) denote the positions of the electrons and nuclei respectively. In theory it would be possible to derive all properties of a system by solving the Schrödinger equation with this Hamiltonian. However, in reality it turns out that an exact solution is only achievable for very small systems and it is therefore necessary to introduce approximations which simplify the problem but still preserve the physical features. In particular, the commonly used Born-Oppenheimer approximation takes into consideration that the dynamics of the nuclei are much slower than the dynamics of the electrons due to larger mass. This means that the nuclear and the electronic degrees of freedom are decoupled from each other and it’s possible to solve for the electronic structure at fixed nuclei positions. The last term in Eq. 4.1 therefore gives a constant contribution to the total energy. However, despite this important simplification the remaining Hamiltonian will still constitute a tremendous challenge due to the many-body nature of the electron-electron interaction incorporated in the second term.

Fortunately, the ability to find approximate solutions the Schrödinger equation for large collection of electrons has increased remarkably during the last decades.

\(^1\)The atomic units \( \hbar = m_e = e = 1 \) are used throughout the chapter.
due to the development of new effective methods together with the boost in computa-
tional resources. This has led to that it’s now possible to treat systems with over 1000 electrons on a regular basis. In the next section we will discuss the basics of the density functional theory (DFT), which is a commonly used method for investigation of the electronic structure.

4.1 Density functional theory

Density functional theory has during the last decades developed into a prominent tool for investigation of the electronic structure in correlated many-body systems. It forms the basis upon which the majority of the calculations in this thesis rest.

4.1.1 The Hohenberg-Kohn theorems

The fundamental core in DFT is the Hohenberg-Kohn theorems [27], which connect the properties of any system of interacting particles in an external potential $V_{\text{ext}}(\mathbf{r})$ to the ground state particle density $n_0(\mathbf{r})$; they state

1. The ground state particle density will uniquely determine the external potential $V_{\text{ext}}(\mathbf{r})$ besides an additive constant. The Hamiltonian is therefore completely defined, except for a constant energy shift, which implies that the many-body wave functions for the ground state and excited states are determined. All properties of the system are thus entirely governed by the ground state density.

2. A functional $E_{\text{HK}}[n(\mathbf{r})]$ can be defined according to

$$
E_{\text{HK}}[n(\mathbf{r})] = T[n(\mathbf{r})] + E_{\text{ee}}[n(\mathbf{r})] + \int d^3 r V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) + E_{\text{II}}
$$

$$
\equiv F_{\text{HK}}[n(\mathbf{r})] + \int d^3 r V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) + E_{\text{II}},
$$

(4.2)

where $T[n(\mathbf{r})]$ is the kinetic energy, $E_{\text{ee}}[n(\mathbf{r})]$ the electron-electron interaction, $V_{\text{ext}}(\mathbf{r})$ is the electron-ion interaction and $E_{\text{II}}$ the ion-ion interaction. $F_{\text{HK}}[n(\mathbf{r})]$ is a universal functional which only depends on the particle density. The exact ground state energy and particle density of the system can be obtained by minimizing $E_{\text{HK}}[n(\mathbf{r})]$ with respect to $n(\mathbf{r})$ under the constraint that the number of electrons $N = \int n(\mathbf{r}) d^3 r$ is kept constant.

The Hohenberg-Kohn reformulation of the many-body theory provides however no guidance for how to construct the functionals of the density. There is also no obvious way on how to relate the kinetic energy operator to the particle density. In order to perform any actual calculations the problem must therefore be rephrased.
4.1 Density functional theory

4.1.2 The Kohn-Sham Ansatz

The main objective of the Kohn-Sham approach is to replace the challenging many-body system with an auxiliary system which allows for a more straightforward treatment. W. Kohn and L. J. Sham showed that the exact many-body ground state particle density can be represented by the ground state of a non-interacting particle system [28]. The Hohenberg-Kohn functional is rewritten into:

\[ E_{KS}[n(r)] = T_s[n(r)] + E_{Hartree}[n(r)] + E_{xc}[n(r)] + \int d^3r V_{ext}(r)n(r) + E_\Pi, \]

\[ E_{xc}[n(r)] = T[n(r)] - T_s[n(r)] + E_{ee}[n(r)] - E_{Hartree}[n(r)], \]

\[ E_{Hartree}[n(r)] = \frac{1}{2} \int d^3r d^3r' \frac{n(r)n(r')}{|r-r'|}. \]  (4.3)

where \( E_{Hartree}[n(r)] \) is the average classical electrostatic repulsion between the electrons and \( T_s[n(r)] \) is the kinetic energy for the independent particles. In this representation all the many-body effects from exchange and correlation have been collected into the exchange-correlation energy \( E_{xc}[n(r)] \). The functional \( E_{KS}[n(r)] \) is minimized when the single particle wave functions \( \psi_i(r) \) satisfy the Kohn-Sham equations

\[ \left[-\frac{1}{2} \nabla^2 + \int d^3r' \frac{n(r')}{|r-r'|} + V_{xc}(r) + V_{ext}(r)\right] \psi_i(r) = \varepsilon_i \psi_i(r), \]  (4.4)

where \( V_{xc}(r) = \frac{\delta E_{xc}(r)}{\delta n(r)} \), \( n(r) = \sum_i f_i |\psi_i(r)|^2 \), \( f_i \) is the occupational number of the Kohn-Sham state \( i \) and \( \varepsilon_i \) are the eigenvalues. The equations map the many-body problem into a mean-field formulation where non-interacting electrons are moving in an effective potential \( V_{eff}(r) \) given by

\[ V_{eff}(r) = \int d^3r' \frac{n(r')}{|r-r'|} + V_{xc}(r) + V_{ext}(r). \]  (4.5)

The total energy of the system is obtained as

\[ E_{KS} = \sum_i f_i \varepsilon_i - E_{Hartree}[n(r)] + E_{xc}[n(r)] - \int d^3r V_{xc}(r)n(r) + E_\Pi. \]  (4.6)

It is important to emphasize that the system of Kohn-Sham equations is non-linear due to the coupling via the particle density and must therefore typically be solved self-consistently using iterative techniques. In principle, the exact ground state particle density and energy can be calculated provided that the exact exchange-correlation functional form is known. However, no explicit form has so far been establish and one has to resort to approximations.

4.1.3 Exchange and correlation functionals

The Kohn-Sham approach separates the kinetic energy of the independent particles and the long-range Hartree interaction into explicit terms. This implies that the
remaining exchange-correlation term can reasonably be approximated as a local or nearly local functional of the particle density and the energy can thus be written as

$$E_{xc}[n(r)] = \int d^3 r n(r) \varepsilon_{xc}(\{n(r)\}, r), \quad (4.7)$$

where $\varepsilon_{xc}(\{n(r)\}, r)$ is the energy density per electron at a point $r$. The accuracy of contemporary DFT calculations rely on the approximations of this energy density.

**The local density approximation**

The natural starting point for many solids is to consider the electron structure as being close to a homogeneous electron gas. In this limit the exchange energy is known exactly while the correlation energy can be fitted to very accurate quantum Monte Carlo simulations carried out by Ceperley and Alder [29]. Based on their data several different parameterizations for the correlation energy have been proposed e.g. by Perdew and Zunger [30] or by Vosko et al. [31].

The local density approximation (LDA) was suggested by Kohn and Sham [28], although the concept was already present in the Thomas-Fermi-Dirac theory in the 1930s. The fundamental idea is to locally approximate the exchange-correlation energy density at each point with the results for the homogeneous electron gas with the corresponding particle density according to

$$E_{xc}^{\text{LDA}}[n(r)] = \int d^3 r n(r) \varepsilon_{xc}^{\text{hom}}(n(r)). \quad (4.8)$$

Overall the LDA is remarkably accurate and tends to reproduce bond lengths, bond angles and vibrational frequencies within a few percent from the experimental values for systems with a slow-varying particle density [32]. The shortcomings of LDA are the tendency to overestimate the binding energy between atoms [33] as well as it often fails when the electrons are strongly correlated as in systems containing d and f orbital electrons [32].

**Generalized-gradient approximations**

The inhomogeneities in the electronic density can be accounted for by extending the exchange-correlation functional to include the gradients of the particle density

$$E_{xc}^{\text{GGA}}[n(r)] = \int d^3 r n(r) \varepsilon_{xc}(n(r), |\nabla n(r)|). \quad (4.9)$$

The first approach in order to evaluate the exchange-correlation energy density is a direct gradient expansion approximation (GEA). It was however realized very early that this will not lead to improved accuracy over LDA since the gradients in real materials are so large that the expansion breaks down. The generalized-gradient approximations (GGAs) were therefore developed with the aim to modify the behavior at large gradients while keeping the desired properties such as sum rules and long-range decay [32]. The GGAs tend to improve binding energies, atomic
4.1 Density functional theory

energies, bond lengths and angles. Different parameterizations for evaluation of \( \varepsilon_{xc}(n(r), |\nabla n(r)|) \) have been proposed e.g. by Perdew and Wang (PW91) \[34\] and by Perdew-Burke-Ernzerhof (PBE) \[35\]. The PW91 and PBE are in many cases regarded as identical despite the fact that they have different analytical forms and are derived in different ways. Indeed bulk properties such as lattice parameters and elastic constants are practically the same but the results in systems where defects or surfaces are included can differ significantly \[36\]. The calculations in this thesis are, with a few exceptions, carried out using the PW91 parametrization.

4.1.4 Implementations

As previously mentioned, the Kohn-Sham formulation of DFT provides a practical scheme to solve the many-body system by mapping it to a system of a non-interacting electrons. In order to solve the differential equations, practical DFT calculations require a procedure for the self-consistency cycle, a basis for expansion of the wave functions and a description of the external potential.

Self-consistent solution of the Kohn-Sham equations

The first step of the self-consistency loop for solution of the Kohn-Sham equations is to make an initial guess for the particle density. This is commonly obtain as a superposition of the non-interacting atomic particle densities. The effective potential is then constructed and the corresponding Kohn-Sham equations are solved. From the calculated wave functions the new particle density is obtained and checked for self-consistency. If the new density differs from the previous step the process must be repeated until self-consistency is achieved. However, if the new density is directly used as input for the next step this will result in a very slow convergence. The new density is therefore typically mixed with the old density, according to some mixing scheme, which can improve the convergence to a large extent. Once self-consistency has been reached the ground state energy can be obtained by using Eq. 4.6.

Plane waves, supercells and pseudopotentials

Before solving the Kohn-Sham equations it’s important to consider which choice of basis set that will provide the most efficient implementation. Using real space atomic-like basis functions is for example the natural choice for calculations of isolated atoms and molecules. However, for systems which can be represented by periodically repeated cells, plane waves constitute a much more suitable basis choice since the Bloch’s theorem is satisfied \[37\]. The wave functions can in this case be written as

\[
\psi_{n,k}(\mathbf{r}) = u_{n,k}(\mathbf{r}) e^{i\mathbf{k} \cdot \mathbf{r}}, \tag{4.10}
\]

where \( n \) is the band index, \( \mathbf{k} \) the reciprocal space vectors within the first Brillouin zone of the periodic cell and \( u_{n,k}(\mathbf{r}) \) is a function with the same periodicity as the system. Using the fact that the periodic function can be expanded in a complete set
of reciprocal lattice vectors $\mathbf{G}$ we have
\[ u_{n,k}(\mathbf{r}) = \sum_{\mathbf{G}} c_{n,k+\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{r}}, \]  
(4.11)
where $c_{n,k+\mathbf{G}}$ are the expansion coefficients. The wave functions can thus be written as
\[ \psi_{n,k}(\mathbf{r}) = \sum_{\mathbf{G}} c_{n,k+\mathbf{G}} e^{i(k+\mathbf{G}) \cdot \mathbf{r}}, \]  
(4.12)
where the sum goes over all reciprocal lattice vectors. For practical implementation the plane wave basis set must be truncated by choosing a cutoff energy $E_{\text{cut}}$ and only include reciprocal lattice vectors satisfying the condition
\[ \frac{1}{2} |\mathbf{k} + \mathbf{G}|^2 \leq E_{\text{cut}}. \]  
(4.13)

The $E_{\text{cut}}$ is determined by systematically increasing cutoff energy until the solution is sufficiently converged.

The above approach requires a periodic cell that can represent the infinite system. Many important systems however, such as liquids or solids with point defects or interfaces, lack this perfect periodicity. The standard procedure is therefore to introduce a so-called supercell, which is an artificial unit cell constructed in such a way that it will capture the essential features of the system. The supercell must be large enough to avoid any spurious interactions between cells but at the same time sufficiently small to be computational affordable. For interfaces where the translational invariance is broken in one direction it’s still possible to create a supercell by using two slabs on top of each other and imposing the periodic boundary conditions in all directions. The slab thicknesses must however be large enough in order to avoid artificial interactions between the two interfaces.

Despite all the advantages the delocalized plane wave basis will fall short when dealing with the tightly bound core electrons. The necessary number of plane waves have to be very large in order to account for the rapidly oscillating wave function behavior near the nucleus leading to tremendous computation time and memory requirements. However, mainly the valence electrons take part in the bonding in materials while the core electrons remain more or less unchanged. It’s therefore possible to introduce effective potentials that describe the true potential from the nucleus and core on the valence electrons in a smoother way. These pseudopotentials are constructed so that the pseudo valence wave functions and potential agree with the wave function and true potential outside a certain cutoff radius. Inside the cutoff the potential is modified for a smoother behavior and thereby the wave function expansion requires a smaller number of plane planes. There exists several types of pseudopotentials, e.g. Norm-conserving [38], Vanderbilt Ultrasoft [39] and PAW [40, 41] which all have their own benefits and disadvantages. All calculations in this thesis are performed using the PAW formalism.
Chapter 5

Boron influence

In order to determine if boron additions to 9-12%Cr steels can reduce the coarsening rate for $M_{23}C_6$ precipitates, it’s necessary to first understand the complexity of the underlying mechanisms. To start with, a general coarsening model for 9-12%Cr steels would have to include the coupled multicomponent diffusion together with the possibility for enhanced diffusion along dislocations, lath- and grain boundaries. It would also be necessary to obtain information about the structure and migration mechanism at the $\alpha/M_{23}C_6$ interface in order to account for any deviations from the local equilibrium conditions. All these features will in turn depend on each other which makes it very hard to separate and to understand the contribution to the coarsening rate from each individual species. A natural starting point is therefore to consider coarsening models which, through various approximations, have reduced complexity but still provide a fundamental understanding of the process.

5.1 Coarsening modeling

The coarsening theory has during the years been extended from dilute binary systems, as discussed in Chapter 2, to include nonideal binary alloys [42] as well as multicomponent systems [11, 43]. In this work we restrict ourselves to consider the coarsening model derived by Ågren et al. [11] and discuss the boron influence based on their approach. The coarsening rate, cf. Eq. 2.16, can be extended to a $M$-component system according to

$$K = \frac{8}{9} \frac{\gamma V^m_\beta}{\sum_{i=1}^M \left( \frac{c_i^\beta - c_i^{\alpha/\beta}}{c_i^{\alpha/\beta}} \right)^2 D_i / RT},$$

(5.1)

where $\gamma$ is the interface energy, $V^m_\beta$ is the molar volume of the precipitate phase, $c_i^\beta$ and $c_i^{\alpha/\beta}$ are the mole fractions of element $i$ for the precipitate and precipitate/matrix interface respectively, and $D_i$ is the diffusion coefficient. It has assumed that the
local equilibrium condition at the interface is satisfied and that there always is a steady state particle distribution in the system.

There have been several different theories proposed on why the increased boron content will decrease the coarsening rate in 9-12%Cr steels. It has been suggested that boron could influence either the interface energy, the metal content or the molar volume for the $M_{23}C_6$ precipitates to a significant extent [22]. The boron content is however evenly distributed in the $M_{23}C_6$ precipitate and the corresponding B/C ratio in the particle is close to the B/C ratio in the steel [25], which in the steels KB and KP is roughly 1/25 and 1/150 respectively [22]. It is thus very unlikely that the small boron amount can have so large influence on either quantities that it can explain the experimental observations.

An alternative explanation is the mass transport through the matrix. By examination of the denominator in Eq. 5.1 we find two different mechanisms. The first possibility involves that the boron atoms themselves can be rate limiting either by a slow diffusion rate or by a small solubility in the matrix. The second option is that the boron instead may influence the diffusion rates for the other elements, which can occur if there is a binding energy between boron and another species. Atom-probe analysis has for example indicated a high probability that boron atoms will be nearest neighbors to molybdenum atoms in the matrix [22, 44].

A third possibility extends beyond the assumptions made in Eq. 5.1. During dissolution and growth there will be a need for local volume changes due the difference in the molar volumes between the precipitate and the matrix. The suggested mechanism [21] is then that when the smaller $M_{23}C_6$ particles dissolve the carbon atoms will go into the favorable interstitial sites in the matrix, which is smaller in size, and thereby produce vacancies. If the boron atoms would to occupy these vacancies the local equilibrium at the interface will be disturbed and Eq. 5.1 does no longer hold. The shortage of vacancies would restrict the possibility to accommodate the local volume change at growing particles leading to slower coarsening rate [21]. At the present stage there has however been no estimations of the number of vacancies that are created or if the boron atoms will combine with them.

In this thesis we direct our focus to the boron mass transport which would be valuable to know before more involved interaction mechanisms are considered.

### 5.2 Boron diffusion

The first approximation in order to understand boron diffusion would be to disregard all possible high diffusion rate paths along dislocations and lath boundaries and restrict the problem to volume diffusion through a perfect martensite phase containing the same composition as the steel. The corresponding multicomponent diffusion equations that arise can in principle be handle by software like DICTRA [45]. Unfortunately the program relies on diffusion databases where boron is not included which poses a direct problem for our purpose. There have been plans to add boron into the databases but a close inspection of the literature has revealed a quite inconsistent picture, based on various experimental studies, even for boron in pure $\alpha$-iron. Nei-
ther the type of solution or diffusion mechanism have been settled [46, 47]. This is probably a direct consequence of the low solubility in the matrix (< 4 ppm) which has made it hard to obtain accurate measurements. In order to acquire a fundamental understanding it is thus necessary to establish the governing boron diffusion mechanism in pure $\alpha$-iron first and then gradually investigate the impact from the interactions with other atom types.

### 5.2.1 Diffusion mechanisms

The two most common diffusion mechanisms in solids are interstitial and substitutional diffusion. The operating mechanism will depend on the type of site the solute atoms occupy in the lattice. The diffusion rate for interstitial atoms in a cubic lattice can be written as

$$D_I = \frac{1}{6} n_I \nu_I r_I^2,$$

(5.2)

where $n_I$ is the number of available nearest-neighbor sites to jump to, $\nu_I$ is the jump rate and $r_I$ is the jump distance. Commonly the interstitial concentration is sufficiently low so that almost every nearest-neighbor sites will be available. In contrast substitutional diffusion mainly occurs through a vacancy mechanism which means that a vacancy must be present at a nearest-neighbor site in order for the atom to be able to move. It will then be necessary to account for the concentration of vacancies in the matrix. The diffusion rate for substitutional diffusion is thus given by

$$D_S = \frac{1}{6} n_S f \nu_S r_S^2 = \frac{1}{6} Z c_v f \nu_S r_S^2,$$

(5.3)

where $f$ is the correlation factor, $Z$ is the coordination number and $c_v$ is the vacancy concentration. At equilibrium conditions the vacancy concentration can be obtained as $c_v = \exp(-G_v/k_B T)$, where $G_v$ is the free energy cost for vacancy formation. The correlation factor arises since there is high probability that the solute atom will make a reverse jump after the first exchange with the vacancy [48].

Each elementary jump between adjacent sites is invoked by thermal fluctuations which will bring the system from a locally stable state across a transition state to another locally stable state, see Fig. 5.1. The corresponding free energy difference $G_m$, associated with bringing the particle from the initial minimum to the saddle point along the reaction coordinate, will constitute a bottleneck for the atomic migration. According to the transition state theory (TST) [49–51] it’s possible to evaluate the jump rate within equilibrium statistical mechanics as

$$\nu_{TST} = \frac{k_B T}{h} \frac{Z^\dagger}{Z} = \frac{k_B T}{h} \exp\left(-\frac{G_m}{k_B T}\right),$$

(5.4)

where $h$ is Planck’s constant while $Z^\dagger$ and $Z$ are the partition functions for the transition state and the initial state respectively. Transition state theory is often combined with the harmonic approximation (hTST) where the vibrations in the system
5 Boron influence

Figure 5.1: The free energy barrier $G_m$ for an elementary jump from a locally stable state across a transition state. The particle moves a distance $r$ during the jump.

are treated as a large collection of harmonic oscillators. The jump rate can then be expressed as

$$\nu^{\text{HTST}} = \nu_0 \exp(-E_m/k_B T), \quad (5.5)$$

where the prefactor $\nu_0$ and migration barrier $E_m$ are given by

$$\nu_0 = \frac{k_B T}{\hbar} \frac{\prod_{i=1}^{N} (1 - \exp(-\hbar \omega_i / k_B T))}{\prod_{i=1}^{N-1} (1 - \exp(-\hbar \omega_i^\dagger / k_B T))}, \quad (5.6)$$

$$E_m = V_m + \frac{1}{2} \sum_{i=1}^{N-1} \hbar \omega_i^\dagger - \frac{1}{2} \sum_{i=1}^{N} \hbar \omega_i. \quad (5.7)$$

Here $\omega_i^\dagger$ and $\omega_i$ are the normal modes of the transition and initial state respectively, $V_m$ the classical potential barrier and $N$ the number of modes in the initial state. It has been assumed that the difference in enthalpy can be approximated with the difference in the internal energy. In the classical limit ($\hbar \omega / k_B T \to 0$) the prefactor reduces to

$$\nu_0^{\text{cl}} = \frac{1}{2\pi} \frac{\prod_{i=1}^{N} \omega_i}{\prod_{i=1}^{N-1} \omega_i^\dagger}. \quad (5.8)$$

In systems where the solute atoms occupy several type of sites simultaneously there can be multiple contributions to the diffusion rate. If the different contributions are treated independently of each other then the diffusion rate can be written as
\[ D = \sum_A P_A D_A, \]  

(5.9)

where \( P_A \) is the fraction of solute atoms occupying site \( A \) while \( D_A \) is the corresponding diffusion coefficient.

### 5.2.2 Diffusion in pure \( \alpha \)-iron

By using density functional theory calculations we have showed that boron atoms form a substitutional solid solution in \( \alpha \)-iron at low temperatures, see Paper I for details. The free energy difference between the substitutional (S) and interstitial octahedral (O) sites is however small (\( \approx 0.1 \) eV) and there will thus be a finite interstitial population in the system. The population depends on the free energy difference and is quite sensitive to the treatment of the vibrational degrees of freedom. In Fig. 5.2 we show the probability for a boron atom to occupy an octahedral site. The results were obtained by using a simple Einstein model for the vibrational degrees of freedom and determining the dynamical matrix for the motion of a boron atom in a frozen surrounding Fe lattice. By including the vibrational degrees of freedom the interstitial population is effectively decreased due to a stiffer environment around the octahedral sites. At 1000 K the population is roughly decreased by a factor ten while at lower temperatures the difference will depend on whether the vibrations are

![Graphical representation](image.png)

Figure 5.2: The probability for a boron atom to occupy an O site with respect to the total number of boron atoms in the \( \alpha \)-Fe matrix. The dashed line shows the result if the vibrational degrees of freedom are neglected.
Table 5.1: Solubilities (in mole fractions) in $M_{23}C_6$ and the matrix [16, 22] together with diffusion coefficients [2] for the main elements in the steels KB and KP.

<table>
<thead>
<tr>
<th>Element</th>
<th>$c_i^\beta$ (KB)</th>
<th>$c_i^\beta$ (KP)</th>
<th>$c_{i/\beta}$</th>
<th>$D_i$ [m$^2$/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>$5.21 \cdot 10^{-1}$</td>
<td>$5.54 \cdot 10^{-1}$</td>
<td>$9.71 \cdot 10^{-2}$</td>
<td>$9.57 \cdot 10^{-20}$</td>
</tr>
<tr>
<td>Mo</td>
<td>$3.50 \cdot 10^{-2}$</td>
<td>$3.10 \cdot 10^{-2}$</td>
<td>$3.22 \cdot 10^{-3}$</td>
<td>$1.72 \cdot 10^{-20}$</td>
</tr>
<tr>
<td>W</td>
<td>$2.00 \cdot 10^{-2}$</td>
<td>$2.00 \cdot 10^{-2}$</td>
<td>$2.38 \cdot 10^{-3}$</td>
<td>$1.48 \cdot 10^{-20}$</td>
</tr>
<tr>
<td>B</td>
<td>$8.34 \cdot 10^{-3}$</td>
<td>$1.37 \cdot 10^{-3}$</td>
<td>$1.4 \cdot 10^{-8}$</td>
<td>-</td>
</tr>
</tbody>
</table>

5.2.3 Influence from defects

A more realistic diffusion model would be achieved by including the effects from the other elements in the martensite phase. If the concentrations from the additional components are sufficiently high this can drastically effect the equilibrium interstitial population as well as the diffusion barrier or the diffusion path.

In order to estimate how large effect the alloying elements can have on the interstitial population we consider a bcc iron matrix with a defect concentration $c_D$ where the defects can for example be Cr, Mo, W or vacancies. We assume that there is a binding energy between the substitutional boron atoms and the defects when they

5 Boron influence
are nearest-neighbors, but neglect all other interactions. If the binding energy is attractive this implies that the interstitial population will decrease since substitutional sites become more energy favorable. The interstitial population can be written as

$$P_O = \frac{g_O \exp(-F_O/k_B T)}{\sum_A g_A \exp(-F_A/k_B T)} = \frac{1}{\sum_A \frac{g_A}{g_O} \exp\left((F_O - F_A)/k_B T\right)}.$$  \hspace{1cm} (5.10)

where $F_A$ denotes the free energy for each site $A$. The sum here includes $A = O, N$ and $S$ corresponding to the octahedral, nearest-neighbor and regular substitutional sites respectively. The term regular in this case refers to all substitutional sites not nearest-neighbor with a defect. The site degeneracies $g_A$ can for low defect concentrations be obtained from a mean field approximation where $g_O = 3$, $g_N = 8c_D$ and $g_S = 1 - g_N$, where the factor 8 is the coordination number for a bcc lattice. We define the binding energy as $\Delta E = F_S - F_N$ and calculate the interstitial population as a function of both defect concentration and binding energy at 600°C, see Fig. 5.4. Here the free energies $F_S$ and $F_O$ are obtained from the boron calculations in pure bcc iron. The results show that in order for the defects to have a significant impact on the interstitial population there must be a large binding energy together with a significant defect concentration. We have however performed density functional theory calculations for these systems which show that the binding energy to Cr, Mo, and W defects is less than 0.1 eV. The typical concentrations in the matrix for these elements are given in Tab. 5.1. For vacancies the binding energy is slightly higher, $\Delta E \approx 0.3$ eV, but in contrast the corresponding concentration at 600°C is
Figure 5.4: The interstitial boron population at 600°C as a function of defect concentration $c_D$ and binding energy $\Delta E$.

very low ($\sim 3 \cdot 10^{-13}$). It is therefore very unlikely that the change in the interstitial population alone can account for a factor $10^5$. 
Chapter 6

Metal-Ceramic interfaces

Understanding the interface between the \((V, Nb)(C, N)\) precipitates and the iron matrix is an important step toward predicting the long-term creep behavior due to V and Nb additions in 9-12\%Cr steels. The interface energetics is expected to govern the nucleation process and to be a contributing factor to the coarsening stability. The two processes give knowledge about the particle number density evolution which is needed when modeling the kinetics of the Z-phase transformation.

6.1 Modeling of interfaces

Real interfaces will in general be very complex and can for example contain segregated atoms, vacancies, dislocations, steps and precipitates. While the interface structure between two solid phases typically can be obtained by various experimental methods there are significant difficulties to carry out direct measurements for the interface energy. First principle calculations therefore constitute a valuable tool in order to access the interface energy and also to distinguish the separate contributions from the different characteristics at the interface. The computational restrictions will however limit the size and complexity of the structures that can be incorporated in the model and approximations must often be introduced.

In theoretical investigations the interface energy for an interface with area \(A\) can conveniently be expressed as

\[
\gamma = \frac{G - \sum_i \mu_i N_i}{A},
\]

where \(G\) is the free energy for the system while \(\mu_i\) and \(N_i\) are the chemical potential and number of atoms respectively for constituent \(i\). The sum \(\sum_i \mu_i N_i\) corresponds to the free energy of the separated bulk phases. This means that the interface energy can be thought of as the excess free energy per unit area due to the presence of the interface. In practice the entropy and pressure-volume contributions to the interface energy are commonly neglected on the basis of them being small [52]. The free energy \(G\) and chemical potentials \(\mu_i\) are then instead replaced by their counterparts in internal energy \(E\) and \(E_i\). This approach is adopted throughout the thesis.
The specific atom species together with their corresponding arrangements at an interface will entirely determine which chemical bonds that can be created between the two phases and thus also the magnitude for the interface energy. An adequate geometry choice is therefore important in order to obtain a realistic description of the energetics. The first approximation for interfaces with specific orientation relationships is commonly to assume them to be both planar and sharp. The planar interfaces can be divided into three categories: coherent, semicoherent and incoherent; determined by the size of the lattice misfit

\[
f = \frac{a^{(1)} - a^{(2)}}{\frac{1}{2} (a^{(1)} + a^{(2)})},
\]

where \(a^{(1)}\) and \(a^{(2)}\) are the lattice parameters for the two phases parallel to the interface plane.

Coherent interfaces arise when the interfacial planes in the two phases have the same atomic arrangements and match perfectly across the interface \((f = 0)\). The semicoherent interfaces have a small atomic misfit \((0 < f \lesssim 0.2)\) and the interface geometry is characterized by periodically recurring misfit dislocations. Coherency is achieved for the majority of the atoms except near the dislocation cores where the structure is highly distorted. Incoherent interfaces are created when the two adjoining phases have very different atomic configurations in the interfacial planes or if the misfit is too high \((f \gtrsim 0.2)\). There will then be no possibility of good matching across the interface and the atoms will be randomly distributed.

In practical DFT calculations with periodical boundary conditions the interface structure must be confined to fit within a finite supercell. This will therefore pose restrictions on how the specific interface can be handled. The standard approach is to first achieve coherency by compressing (or expanding) the two phases to yield a common lattice parameter. A three dimensional potential energy surface \(\gamma(R)\) can then be calculated according to

\[
\gamma(R) = \frac{1}{2A} \left( E(R) - \sum_i E_i N_i \right),
\]

where \(R\) is a relative displacement vector between the two phases while the factor 2 arises since there are two interfaces present in the supercell. The potential energy surface is then used to obtain the interface energies for the coherent and incoherent cases. The former is directly given by the minimum value while a reasonable approximation for the incoherent interface can, due to the random nature, be obtained as the mean value over the entire surface. For a semicoherent interface the interface energy will end up somewhere between the coherent and incoherent limits where the exact value will depend on the energy cost to create the misfit dislocations. To include the dislocation structure entirely in DFT calculations would be too computational demanding since the dislocation periodicity will typically be large especially for small misfits \((\sim 100 \text{ Å})\). The alternative route is instead to resort to methods which combine the accurate treatment for the electronic structure from
DFT together with elasticity theory to account for the displacements near the dislocation cores. In Paper II we utilize such an approach and combine DFT with a Peierls-Nabarro model in order to investigate semicoherent interfaces between iron and nacl structured carbonitrides.

6.2 Precipitates

In reality precipitates have a finite extension which means that the translation invariance within the interface plane, which is assumed in the DFT calculations, will be broken at the edges and that the particle in general will be bounded by multiple interfaces. From a pure interface energy perspective it would always be more favorable to create coherent interfaces toward the surrounding matrix. However, there is not always the possibility to find a lattice plane that is common to both phases. Quite often there is only one such specific plane that is more or less identical which leads to that a coherent or semicoherent interface is formed in a certain direction while the other interfaces will be incoherent. Relatively large VN precipitates are for example found as thin discs having a distinct orientation relation for the circular area, with a semicoherent behavior, but an incoherent nature for the rim [53], cf. Fig. 6.1.

In order to obtain an accurate model for precipitates we must take into consideration that the shape and boundary structure don’t need to remain constant during growth. Depending on the elastic distortions that is built up in the environment

Figure 6.1: HREM image of a VN disc embedded in the iron matrix from [53] showing the (110)$_{\text{Fe}}$ and (111)$_{\text{VN}}$ lattice fringes. The arrows indicate the locations of two misfit dislocations. The vertical bar corresponds to 6 nm.
during the nucleation and growth processes, transitions from one specific boundary structure to another may occur. The equilibrium structure will be reached when the sum of the elastic and interface energy contributions is at minimum i.e.

\[ V_\beta (G_{el} + G_{coh}) + \sum_i A_i \gamma_i = \text{minimum}, \]

(6.4)

where \( G_{el} \) is the elastic energy cost per volume unit for the induced elastic distortions caused by the difference in molar volume between the matrix and the precipitate. For finite size precipitates there is also the possibility to create a coherent interface, even when there is a small misfit, by straining the phase into coherency with the surrounding matrix. The energy cost associated with the required strain is denoted by \( G_{coh} \). Note that for semicoherent and incoherent interfaces \( G_{coh} = 0 \) since the phase is not strained at all in these cases. If we now for example would assume that the \( G_{el} \) term is essentially the same for both a coherent and a semicoherent interface at a given shape, this will imply that a transition can occur between the two structures when the energy costs for the coherency strains exceed the gain in the interface energy. In general we must nevertheless account for any volume or shape changes and the \( G_{el} \) term must be included. According to Nabarro \[54\] it’s possible to express the strain energy \( G_{el} \) for incompressible spheroids with the semiaxes \( a, a, b \) as

\[ G_{el} = \frac{2\mu_{Fe}}{3} \left( \frac{V_\beta^m - V_{Fe}^m}{V_{Fe}^m} \right)^2 E(b/a), \]

(6.5)

where \( \mu_{Fe} \) is the shear modulus for iron, \( V_\beta^m \) and \( V_{Fe}^m \) are the molar volumes and

---

Figure 6.2: The shape depending factor as a function of the precipitate shape from [54]. Here \( a \) denotes the equatorial diameter and \( b \) the polar diameter.
$E(b/a)$ is a shape depending factor. The analysis shows that disc-like particles will be more favorable, as they require a lower elastic energy per volume unit to incorporate into the matrix than spheres with the same volume, cf. Fig. 6.2. The effect must however always be put in relation to the magnitude of the interface energies in order to deduce the final impact on the equilibrium structure.
Chapter 7

Summary and Outlook

The aim of this thesis has been to obtain a better understanding of the precipitation of carbonitrides in steels by using first-principles calculations based on density functional theory. The formation and stability of these precipitates play a vital role for the creep strength of the steel.

In particular, we have investigated if boron diffusion through the iron matrix can have any important effect on the coarsening rate of $M_{23}(C,B)_6$ particles ($M =$ transition metal). The results show that boron predominantly forms a substitutional solid solution in bcc iron at low temperatures. However, the energy difference between the substitutional and the octahedral interstitial sites is found to be small so at elevated temperatures there will be a finite interstitial population. As a consequence boron diffusion under equilibrium conditions will be governed by the interstitial mechanism. The corresponding diffusion rate is too fast to allow for an explanation of the experimental observations that increased boron content will decrease the coarsening rate of the $M_{23}(C,B)_6$ particles. The effect from commonly occurring alloying elements such as Cr, Mo and W on the boron diffusion was therefore also considered but it was concluded that the influence would not be sufficient in order to change the previous conclusion.

In addition, the energetics for the semicoherent interfaces between the iron matrix and nacl structured MX precipitates ($X = C$ or N) were studied by using density functional theory calculations in combination with a Peierls-Nabarro model. The chemical interactions across the interface were explained in terms of covalent Fe(3d)-X(2p) and metallic Fe(3d)-M(d) bonds, where the strength of the metallic interaction was connected to the relative position of the M d-band and Fe d-band centers. We also showed that the elastic energy contained in the dislocation network, due to the lattice misfit, gives a significant contribution to the interface energy.

The results in this thesis provide a starting point for further investigations of the coarsening process of $M_{23}(C,B)_6$. The present calculations for the boron diffusion have so far assumed that the equilibrium boron distribution always is achieved at all times, but in reality this may not be the case. In particular, the possibility that vacancies are created during dissolution of small $M_{23}(C,B)_6$ precipitates, as discussed in Chapter 5, constitutes such a situation. If a sufficient number of vacancies are produced this can disturb the boron population since there will be an increased
probability to occupy the substitutional sites. The interstitial population can in turn decrease substantially and boron diffusion may thus be governed by a substitutional mechanism. In future work we will therefore in more detail investigate the dissolution of the M_{23}(C,B)_6 precipitates and how that may influence the boron diffusion.

Another interesting issue is to understand the formation of the Z-phase in 9-12%Cr steels, which has a detrimental influence on the creep strength. While the Z-phase, in addition to chromium, contains the same elements as the MX precipitates, it has not been observed to nucleate on its own in the matrix [17]. This have been explained in terms of a much faster MX nucleation during tempering which drains the required alloying elements from the matrix. The Z-phase instead develops first during service operation but is however always found in physical contact with pre-existing MX phases, which indicates that it either only can nucleate on the MX interface or is formed by chromium diffusion into the MX particles [17]. In order to understand why the Z-phase can’t nucleate directly it would be important to first compare the energetics between the Fe/Z-phase and the Fe/MX interfaces. Since if the interface energies will be significantly higher for the Fe/Z-phase interface than for the Fe/MX interface, this could explain why Z-phase is so hard to nucleate due to the strong dependence of the interface energy in the nucleation process. For completeness it would also be necessary to include the elastic distortions in the matrix arising from the precipitate, for example by using a continuum description.
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Bibliography


Paper I

Nature of boron solution and diffusion in α-iron
D. H. R. Fors and G. Wahnström
Paper II

Interface energy trends for semicoherent Fe(001)/MX(001) systems using
*ab initio* calculations
D. H. R. Fors and G. Wahnström
(in manuscript)