The inheritance of different microstructures found after hot rolling on the properties of a completely annealed DP-steel

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1. Introduction

1.1. Background on Dual phase steel

Dual phase steel is a material which consists of martensite islands embedded in a ferrite matrix. Usually the martensite volume fraction lies between 15% and 20% [1]. Typical compositions of this class of steel can be found in Table 1. The production process of commercial material is often divided into two steps (cf. Figure 1-1). After hot rolling, coiling and cold rolling (Step 1), a second heat treatment is applied to the material (Step 2). This heat treatment is called intercritical annealing (ICA). During this intercritical annealing the desired volume fraction of ferrite and martensite is obtained. The plateau temperature lies here in the two phase region of austenite (γ) and ferrite (α). Over the past thirty years there has been an increasing interest in understanding the relation between the microstructure found after hot rolling and the properties of the completely processed dual phase steel [2-9].

The present work deals with one aspect of this relationship, the inheritance of the substitutional element distribution through the annealing process.

![Figure 1-1: Schematic time temperature diagram of the production process of the dual phase steel. CR means cold rolling, ICA means intercritical annealing and HR hot rolling.](image)

<table>
<thead>
<tr>
<th>Steel</th>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Si</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.06C-1.5Mn</td>
<td>0.06</td>
<td>1.47</td>
<td>0.009</td>
<td>0.010</td>
<td>0.23</td>
<td>0.009</td>
</tr>
<tr>
<td>0.12C-1.5Mn</td>
<td>0.12</td>
<td>1.47</td>
<td>0.009</td>
<td>0.010</td>
<td>0.24</td>
<td>0.008</td>
</tr>
<tr>
<td>0.20C-1.5Mn</td>
<td>0.20</td>
<td>1.53</td>
<td>0.009</td>
<td>0.010</td>
<td>0.25</td>
<td>0.023</td>
</tr>
</tbody>
</table>

Table 1: Typical average compositions of dual phase steel [10].

1.2. Influence of different microstructures after hot rolling on the properties of the fully processed dual phase steel

In order to reveal in detail the influence of the microstructure obtained after hot rolling, on the properties of dual phase steel, one has to apply the same intercritical annealing process.
on steels with different microstructures, but the same average composition. The following section is divided into three parts. First it will be shown how different phases are formed in as hot rolled material. Afterwards the influence of the phases will be discussed. The last part will deal with the impact of the local composition of substitutional elements on the properties of dual phase steel.

It is known that the coiling temperature influences the microstructure of hot rolled material [11]. Mohatny et al showed, for example, that low alloyed carbon steel (0.08C 2.0Mn-Cr-Mo) coiled at 650 °C consists of ferrite and pearlite, but a coiling temperature of 550 °C leads to bainitic ferrite and islands of martensite.

As described by several authors, a ferrite + pearlite microstructure tends to form austenite more slowly during intercritical annealing compared to a microstructure consisting of martensite, bainite, pearlite and ferrite [2, 3, 12]. This can lead to different contents of martensite. The effect of the martensite fraction on the mechanical properties of dual phase steel has been demonstrated by a number of studies [13-15]. In general an increased content of martensite leads to a higher yield and tensile strength.

The inhomogeneous distribution of substitutional elements influences the phase transformation occurring in steel as well as the mechanical properties of the material. Thereby, it has to be distinguished between micro segregation of substitutional elements, caused by segregation during solidification ([16] p. 27), and enrichments initiated by carbides. The former ones are found in the form of banded structures. Pearlite, bainite or martensite are often found in bands with a high Mn content [7-9, 17]. Its effect on the mechanical properties is limited to the ductility and the impact energy [18]. On the micro to nanometre scale high Mn concentrations can be found in cementite, which is known to enrich with substitutional elements [6, 19-22]. Song et al. investigated the level of Mn enrichments in carbides in dependence on the average Mn concentration [19]. They applied the same heat treatment on two different steels, one with a low Mn content and one with a higher one. The carbides present in the high Mn steel enriched 2.5 times more with Mn than in the low Mn steel and were distributed finer in the matrix. This leads to a smaller ferrite grain size as well. The effect of these small particles enriched with Mn on the completely processed steel is rarely discussed. Cai et al. showed the evolution of Mn enrichments, caused by pearlite, during reaustenization of dual phase steel [6]. After the heat treatment applied to the material, the carbides were dissolved and a duplex microstructure consisting of ferrite and austenite/martensite was obtained. The martensite had a higher Mn content than the ferrite. It is not clear whether this was caused by the original Mn enrichments or by the equilibration of Mn between ferrite and austenite. The role of globular cementite during the formation process of dual phase steel is described by Calcagnotto et al. [23]. They intercritical annealed
two steels which differed only in the average content of Mn. Before the thermal processing the carbides present in both steels were enriched with Mn. Afterwards the martensite islands were found at places of higher Mn content, which had been austenite during the intercritical annealing. Mn is known to increase the hardenability of austenite [24]. It lowers the temperature at which austenite transforms to another phase. This effect was only significant for high Mn steels and not for low Mn steels, since only in the case of high Mn steels cementite was enriched strongly enough with Mn to raise the hardenability of the austenite significantly.

1.3. Motivation and aim of the thesis

The primary purpose of this thesis is to obtain a deeper understanding how different microstructures after hot rolling influence the properties of dual phase steel. Particular attention is paid to the role of segregation of substitutional elements caused by iron (Fe) carbides. The investigations were carried out on commercially-processed dual phase steel as well as on hot rolled material which has been processed in the laboratory (in-lab processed). For both steels two variants were selected. They had the same average composition but the coiling temperature was different. It could be shown in the course of the thesis that this led to different degree of enrichment of Mn in the carbides. The variant coiled at a higher temperature is named pearlite plus ferrite microstructure (P+F). The material coiled at a lower temperature is called bainite plus martensite (B+M). In order to study the influence of different hot rolled microstructures, the following heat treatment was the same for both variants. Different experimental methods in combination with theoretical simulations were used to study the behaviour of the material. It should be mentioned that the applied heat treatment does not correspond to an intercritical annealing, since the plateau temperature is in the pure austenite region. Intercritical annealing refers to a heat treatment which is in the two phase region of austenite and ferrite.

In Chapter 2 the theoretical fundamentals of the physical processes necessary to understand the behaviour of the material during thermal heat treatment are explained. The background of the used experimental techniques is detailed where necessary. The focus lies here on the phase transformation in equilibrium, phase transformation out of equilibrium, the basics of X-ray generation in material used for x-ray spectroscopy in the scanning electron microscope (SEM) and on the formation of electron backscatter diffraction (EBSD) patterns for crystallographic measurements in the SEM. X-ray generation is explained in detail, since x-ray spectroscopy is one of the techniques frequently used during this study.

Chapter 3 describes the experimental methods used during this thesis. This comprises not only the thermo mechanical process applied to the material and the experimental techniques
used for analysing it, but also the simulation methods which helped to understand the experimental results.

The 4th chapter presents the results of the in-lab processed material and discusses them. It is divided into 4 main parts. The first section deals with the results of the experiments performed on the in-lab processed steel. In the second section of this chapter, the results of the experiments are discussed and open questions are addressed. Some of these open questions are answered in the third section. Here, the results of thermodynamic simulations are presented. They were performed using DICTRA and Thermo-Calc and help to understand the evolution of the local Mn content during the heat treatment and its influence of the local phase transformation, which leads to a better understanding of the transformation behaviour of the material during the heat treatment and the related mechanical properties. In the last part a conclusion of all performed experiments and simulations is given and the different influences on the properties of the examined steel are addressed.

In the 5th chapter the results of the commercially-processed material are presented. In order to perform the analyses, which are necessary to understand the properties of the material, the same techniques were used as for the laboratory-processed material. Here, all measurements were performed after complete heat treatment. At the end of this chapter, the results of the commercially-processed material are compared with the results of the laboratory-processed material. The comparison showed that laboratory-processed and industrial material show the same basic behaviour. The lab experiments can therefore be used to discuss the mechanisms proceeding in the industrial material.

The experimental results from chapter 4 suggested that the material contains different varieties of ferrite, depending on the particular thermal history of the material. The 6th chapter therefore addresses the question, how ferrite in a dual phase steel is influenced by its formation temperature. To this end, a low C steel was completely reaustenized and quenched to different temperatures at which ferrite started growing. Afterwards, EBSD measurements were performed in order to obtain the geometrically necessary dislocation (GND) density from the local lattice curvature. The results of these measurements are discussed in terms of the formation mechanisms of ferrite. It is shown how they can be related to a change of the growth regime of ferrite.

A Summary and an outlook are presented in the 7th chapter. As an outlook it is shown, how Mn enrichments caused by carbides could be used to taylor the mechanical properties of steel.
2. Theoretical background

2.1. Diffusion in solids

In solids the position of single atoms is fixed. Due to thermal activation it is possible for atoms to leave their original position and change to another place in the crystal lattice ([25] p. 155). One of the first equations describing the movement of an element in dependence of the concentration gradient ($\frac{dc}{dx}$) is Fick's first law ([25] p.155):

$$j_D = -D \frac{dc}{dx} \quad (2.1)$$

Here, $j_D$ is the diffusion flux. It describes the amount of atoms which are passing through a unit area in a specific time. The diffusion constant $D$ links the concentration gradient to the movement of the atoms. $D$ increases with rising temperature, as can be seen in Figure 2-1. The diffusion constant does not only depend on the temperature of the system but also on the diffusing element. C for instance, diffuses much faster in ferrite compared to Mn. The main reason for this is the different size of the atoms and the different amount free neighbouring lattice sites. In general it can be distinguished between diffusion of substitutional elements and diffusion of interstitial elements. Both processes will be presented in the following chapter.
2.1.1. Diffusion mechanisms

For the diffusion of substitutional elements, for example Mn or Cr in an Fe matrix, vacancies play an important role. Since substitutional elements have a comparable size to the matrix, they can only occupy similar sites in the crystal structure as the matrix atoms. If the neighbouring positions of an atom are occupied, it cannot change its position. The movement is only possible, if one of the neighbouring lattice sites is empty, i.e. corresponds to a vacancy. In Figure 2-2, the mechanism is shown schematically. There is an activation energy needed for the atom to exchange its position, since it has to cross a potential wall. This wall is caused by the fact that during the movement, the atom occupies positions that do not correspond to its equilibrium position.
2. Theoretical background

Interstitial elements, as the name implies, do not occupy positions on the lattice of the matrix phase but those in between. This is possible because the size of the interstitial atoms is significantly smaller than that of the lattice atoms. They have their own sub lattice consisting of interstitial lattice sites (cf. Figure 2-3). The energy barrier that has to be passed during the change of position is comparable to the diffusion of substitutional elements. However, the chance that a neighbouring position is occupied by a vacancy is much higher. This leads to a faster diffusion of interstitial atoms compared to diffusion of substitutional elements.

Figure 2-3: Principle of the interstitial diffusion ([26] p. 349)

2.1.2. Diffusion in multicomponent systems

For a one-phase binary alloy at constant temperature and pressure, Fick’s 1st and 2nd law can be written as follows:

\[ J_k = -D_k \frac{\partial c_k}{\partial x} \quad \text{and} \quad \frac{\partial c_k}{\partial t} = D_k \frac{\partial^2 c_k}{\partial x^2}. \]  

(2.2)

Here, \( J_k \) is the amount of transported atoms of type k per unit time and per unit area of the cross-section perpendicular to the diffusion direction, \( \frac{\partial c_k}{\partial x} \) describes the change of the concentration profile with the position, \( \frac{dc_k}{dt} \) describes the change of the concentration in with
time and $D_k^r$ is the interdiffusion coefficient of the element k [27]. If the diffusion in a system containing more than two elements is described, Fick’s laws have to be extended.

The main driving force for diffusion is the minimization of the free enthalpy of a system. Here, the chemical potential of every species has to be taken into account. For multicomponent systems, this has been done by Onsager et al [28, 29]. Assuming a constant temperature and pressure in the material, the total flux for all different elements can be described as follows [27].

$$J_k = -\sum_{i=1}^{n} L_{ki}^r \frac{\partial \mu_i}{\partial x}$$

$\mu_i$ are the chemical potentials for the different elements and depend on the composition. $L_{ki}^r$ is a proportionality factor which depends on the mobility of the species. Rewriting this equation in dependence of the concentration leads to:

$$J_k = -\sum_{j=1}^{n} D_{kj} \frac{\partial c_j}{\partial x} \text{ with } D_{kj} = \sum_{i=1}^{n} L_{ki}^r \frac{\partial \mu_i}{\partial c_j}$$

(2.4)

Where in $L_{ki}^r$ is the kinetic part of the diffusivity and $\frac{\partial \mu_i}{\partial c_j}$ the thermodynamic part of the equation. With the commercial software package DICTRA it is possible to solve the flux equation [30] [27]. The required kinetic data is included in a database, which is based on experimental data.

2.1.3. Calculation of diffusional phase transformations using DICTRA

If a phase transformation is accompanied by a change of composition and / or a non-coordinated movement of atoms across the phase boundary, it is called a diffusional phase transformation. The boundary between the growing phase and the shrinking phase is called the phase boundary. Its movement is for diffusional phase transformations controlled by diffusion. For materials which are alloyed with substitutional elements as well as with interstitial elements, there are different ways to calculate a diffusional phase transformation. They are distinguished by the kind of thermodynamic equilibrium established at the phase boundary. Local equilibrium means that the chemical potential of all elements is the same on each side of the phase boundary [27]. The three different local equilibria which can be established are the local equilibrium with partitioning (LE), local equilibrium with negligible partitioning (LENP) and paraequilibrium (PE). A computer simulation tool capable of simulation diffusional phase transformations is DICTRA [30].

Most parts of the three following sections are a summary of Chapter 1 of the book ‘Continuum Scale Simulation of Engineering Materials’ [31].
2.1.3.1. **Local equilibrium with partitioning (LE)**

The concept of LE will be explained by using the example of the transformation of austenite to ferrite in steel. Local equilibrium is expressed by equality of the chemical potentials ($\mu$) for all elements at the boundary between ferrite and austenite $\gamma/\alpha$

$$\mu_k^{\alpha/\gamma} = \mu_k^{\gamma/\alpha} \text{ for } k = 1, 2, \ldots, n.$$ (2.5)

where $n$ is the number of elements involved ([31] p. 12). The degrees of freedom in a system can be calculated using Gibbs phase rule. For a 2-phase equilibrium, the degree of freedom is $n - 2$, if temperature and pressure are constant. This means that for the binary system Fe-C, the degree of freedom is 0. This implies that the LE is identical with the global equilibrium, which leads to the fact that on both sides of the phase boundary the composition is fixed by the phase diagram. In case of a system with more than two elements, the degrees of freedom is larger than 0. This means that one can find many tie-lines in a multicomponent phase diagram, which fulfil the LE condition. In order to find the operating tie-line, the following boundary condition has to be taken into account. According to Borgenstam et al. [27] the mass balance across the phase boundary in a system containing ferrite ($\alpha$) and austenite ($\gamma$) can be written as follows:

$$J_k^{\alpha} - J_k^{\gamma} = \frac{v^{\alpha}}{V_M^{\alpha}} (x_k^{\alpha} - x_k^{\gamma}) \text{ for } k = 1, 2, \ldots, n - 1.$$ (2.6)

Where $J_k^{\alpha}$ and $J_k^{\gamma}$ are the fluxes of the element $k$ over the boundary, $x_k^{\alpha}$ and $x_k^{\gamma}$ are the contents of component $k$ in $\alpha$ and $\gamma$ in mole fraction close to the phase boundary, $v^{\alpha}$ is the velocity of the boundary and $V_M^{\alpha}$ is the molar volume of the $\alpha$-phase. With this equation it is possible to calculate the migration rate of the interface for different elements and concentration levels at both sides of the interface. As a boundary condition it is determined that the migration rate of the elements hast to be the same for all elements. The boundary tie line which fulfils this condition is the operating tie line of the system. It depends on this tie line if partitioning of all alloying elements is necessary or not. Figure 2-4 shows an isothermal section through the phase diagram of Fe-Mn-C at 1000 °C. Additionally an isoactivity line for C is shown. For all composition laying on this line the activity of C is the same. For all compositions located in the upper shaded region, labelled "LE", the growth regime follows the local equilibrium condition with partitioning. All compositions have the same activated tie line (LE-tie-line), which requires a partitioning of C and manganese (Mn) during the growth of ferrite, since the starting alloy composition is different in terms of Mn and C from the composition of the growing ferrite.
2.1.3.2. **Local equilibrium with negligible partitioning (LENP)**

If the alloys are below alloy (4), the operating tie line does not require a partitioning of Mn. This is due to the fact that the operating tie line needs the same Mn content in the growing ferrite and in the existing austenite. Only at the boundary between austenite and ferrite, a spike of Mn exists, whereby its height is defined by the intersection of the operating tie line with the pure austenite region. C does still partition between austenite and ferrite. DICTRA can calculate the transition from LE to LENP automatically, not only for a 3 component system, but also for systems with more than 3 components.

2.1.3.3. **Para equilibrium (PE)**

Para equilibrium describes the diffusion in the case where the substitutional elements are immobile compared to the speed of the interface, because the temperature is too low. In this cases, it is not possible for the substitutional elements to follow the velocity of the moving phase boundary and equilibrium cannot be established with respect to these elements. For interstitial elements like C it might be still possible to diffuse fast enough to follow the moving boundary. This was at first discussed by Hultgren in 1947 [32]. To establish for this case the boundary conditions the system is treated as a pseudo binary system M-C, whereby indicates M all substitutional elements together. The Gibbs energy of this system has to be constructed in such a way that it is the same as for the system Fe-X-C with X being a substitutional...
2. Theoretical background

As shown by Schneider et al. ([31] p. 12), the boundary conditions for the simulation are:

\[ \mu_C^\alpha = \mu_C^\gamma \text{ and } \mu_{Fe}^\alpha \mu_{Fe}^\alpha + \mu_X^\alpha \mu_{Fe}^\alpha = \mu_{Fe}^\gamma + \mu_X^\gamma \mu_{Fe}^\gamma. \]  \hspace{1cm} (2.7)

The first equation describes the local equilibrium for C over the boundary and the second one shows that the fraction of a substitutional element X and Fe has to be constant in both phases. The u-fraction is defined as the site fraction of an element with reference to the substitutional sublattices only. A phase diagram, which follows out of this, can be seen in Figure 2-5. The resulting tie lines are horizontal, when the concentrations of the substitutional elements are in u-fraction. The PE reaction does not lead to the same equilibrium phase fractions as it is possible with LENP or LE. At the end of the reaction, only C has the same chemical potential on both sides of the phase boundary, but the substitutional elements do not. It is possible to simulate a reaction according to PE with DICTRA but it has to be activated manually since it does not follow directly out of the thermodynamics as LE and LENP do.

**Figure 2-5:** Para equilibrium phase diagram superimposed onto the full equilibrium diagram. ([31] p. 13)

### 2.2. The system Fe-C

The basis of all steels is the binary system of Fe and C. Here, the Fe rich part of the system is of greater interest. Since in technically relevant steels only the metastable phase cementite and not graphite is produced, the metastable phase diagram of Fe C will be discussed. Here, pure Fe has 3 stable phases, α-iron (ferrite, bcc), γ-iron (austenite, fcc) and δ-iron (δ-ferrite, bcc). Steel is defined as an alloy of Fe and C with a C content lower than 2.06 wt. %.
C atoms are significantly smaller than Fe atoms and fit into the interstitial lattice sites of the different Fe phases. Thereby, it depends on the size of the interstitial lattice sites, how much C can be solute in a given face. Since austenite (fcc) has bigger interstitial lattice sites than ferrite (bcc) ([34] p. 25), the solubility of C is higher in austenite compared to ferrite (cf. Figure 2-6). If the material consists of both, Fe and C, the metastable phase cementite can be formed. Cementite consists of 6.67 wt. % C and 93.33 wt. % Fe. In order to explain the formation of the different phases in dependence on the temperature in more detail, a very slow cooling down of a steel consisting of 0.2 wt. % C and 99.8 wt. % Fe will be discussed according to the phase diagram of Fe and C. The starting temperature lies at 1000 °C. At this temperature the entire steel is austenitic. Once the two phase region of austenite and ferrite is reached, proeutectoid ferrite starts growing. The equilibrium concentration of C in both phases can be determined from the tie-lines in the phase diagrams. In the case of a two-phase equilibrium the fraction of both phases can be derived using the lever rule ([26] p. 317). In the two phase region of ferrite and austenite the lever rule is expressed as follows:
\[ \frac{N_a}{N_0} = \frac{a}{a + b} \quad \text{and} \quad \frac{N_\gamma}{N_0} = \frac{b}{a + b} \]  

(2.8)

In these equations, \( N_a \) is the amount of atoms belonging to ferrite, \( N_\gamma \) is the amount of atoms belonging to austenite, \( N_0 \) is the total amount of atoms and \( a \) and \( b \) are defined in Figure 2-7.

Once the material has cooled down to the eutectoid point of austenite, ferrite and cementite, the present austenite transforms into pearlite, a lamellar mixture of ferrite and cementite.

Figure 2-7: Section of the Fe C phase diagram calculated with Thermo-Calc. The black vertical line indicates the C concentration in the assumed type of steel. Using the lever rule at 800° C, leads to 43 at. % ferrite and 57 at. % austenite.

2.3. The system Fe-Mn-C

Mn is one of the most important alloying elements in steel ([33] p. 169). It is used to deoxidize the steel melt and to prevent the formation of Fe sulphides by forming Mn sulphides instead. The equilibrium concentration of Mn between melt and growing crystal varies with decreasing temperature. Therefore, Mn is enriched locally during dendritic solidification in so called micro (or crystal) segregations. During hot rolling these inhomogeneously enriched dendrites are elongated, which leads to an elongation of chemical heterogeneities into the rolling direction as well.

2.3.1. The austenite stabilizing effect of Mn

The formation of austenite is also influenced by the presence of Mn. It is an austenite stabilizing element, which means that the austenite phase becomes more stable at lower temperatures ([34] (p. 74)). This can be seen in the phase diagram of Mn and Fe (cf. Figure
2.8. It is calculated for a C content of 0.2 wt. %. The enrichment of cementite in pearlite with Mn will be discussed in the next chapter.

![Figure 2-8: Phase diagram of Fe-Mn with 0.2 wt.% C calculated with Thermo-Calc.](image)

**2.4. The decomposition of austenite**

2.4.1. The growth of pearlite

The following section is a summary of [34] Chapter 4. Other sources will be referenced where necessary. While cooling down, pearlite starts growing once the two phase region of cementite and ferrite is reached. For alloys containing Mn pearlite starts occurring when the three phase region of austenite, ferrite and cementite is reached. Here, pearlite preferentially nucleates at austenite boundaries. This reaction is entirely diffusional in nature. At the beginning of pearlite formation a ferrite nucleus is formed, which leads to a C enrichment of the adjacent austenite. When the concentration level in austenite is sufficiently high, it transforms into cementite. Next to this newly formed cementite the austenite is depleted of C which will trigger ferrite formation again. This procedure leads to the lamellar arrangement of ferrite and cementite (cf. Figure 2-9). In front of the pearlite package, C is distributed in a way that the growth of ferrite and cementite is slowed down. Transverse diffusion is needed to transport the C in front of the ferrite to the growth front of the cementite. This allows the pearlite to grow into the austenite. With a higher undercooling of the austenite, the lamellar spacing between two cementite lamellae shrinks. The lamellar spacing can be calculated using the following empirical equation:
\[ \lambda \approx \frac{15}{\Delta T} \]  

(2.9)

Here, \( \lambda \) is the lamellar spacing of the pearlite while \( \Delta T \) is the undercooling of the austenite. Mn influences the formation of pearlite in different ways. As shown in the previous chapter, Mn stabilizes the fcc-phase to lower temperatures. By taking equation (2.9) into account, it is obvious that pearlite grown at the same temperature has a higher lamellar spacing, if the austenite is enriched with Mn, provided that the factor of 15 is not changing. It is known that cementite has a high solubility of Mn [21, 22], which has been also observed during the formation of pearlite [6, 20, 35, 36]. Even though it is accepted that Mn can redistribute during the growth of pearlite, it is still under discussion, whether pearlite can grow without the partitioning of Mn. Razik et al. investigated the redistribution of Mn during the growth of pearlite in dependence of temperature [35]. The used material was a ternary steel consisting of Fe, Mn and C. They found that the equilibrium partition coefficient decreases with increasing temperature. Additionally they discovered a temperature, below which no partitioning occurred any more. This lower limit depends on the composition of the particular type of steel. In contrast to these results, Al-Salman et al. did not find such a temperature [20]. Their experiments were performed on a Fe-Cr-Mn-C alloy. It was shown as well, that the substitutional elements keep on partitioning even after the formation of pearlite. Bhadesia et al. reviewed the formation of pearlite for different ternary alloys [37]. They were not able to calculate the growth rate of pearlite correctly, without taking partitioning of substitutional elements into account.
2.4.2. The growth of bainite

The following section is a summary of [34] p. 183 and following. Bainite is a mixture of a matrix with bcc crystal structure and a second phase with high C content. The latter is usually cementite. It is formed when the temperature reaches a certain point, at which the diffusional formation of pearlite is no longer possible. This temperature range is normally between 550 °C and 250°C. At this stage, the austenite transforms displacively into ferrite, which is similar to the formation of martensite. A displacive phase transformation implies the coordinate movement of atoms usually mediated by interface dislocations. In dependence on the formation temperature, bainite is classified as upper bainite and lower bainite.

The upper bainite is formed at higher temperatures (550°C – 400°C). There are two different growth mechanisms, which depend on the C content. For lower C concentrations, a part of the austenite transforms displacively into a ferrite lancet. Afterwards, the C can still diffuse short ways and accumulates between two ferrite lancets and forms cementite. For higher C contents, the diffusional formation of cementite is the first to begin. As a result, the austenite depletes of C. This continues until MS is reached. Now the austenite transforms into bcc.

The lower bainite is formed between 400°C and 250°C. Similar to the upper bainite, bcc is formed displacively out of the austenite. Due to the lower temperature, the diffusivity of C is decreased and it is no longer possible for the C to diffuse out of the ferrite. Instead of this, carbides are formed inside the ferrite plates.
Bainite is still a subject of ongoing research and aspects like carbide free bainite have not been mentioned here (For detailed discussion see Bhadeshia et al. [39]).

2.4.3. The growth of martensite

The transformation of fcc-iron to bcc-iron can also occur without diffusion. This so-called martensitic transformation takes place, when austenite is strongly undercooled. Due to the low temperature, diffusion is very limited. In contrast, the driving force for the phase transformation of fcc to bcc is strongly increased. This can lead to a displacive transformation of the fcc structure into the bcc structure. Analysing two fcc cells lying next to each other reveals, that one virtual bcc cell is already at place, while the lattice parameters are \( c_v = a_A \) and \( a_v = \frac{a_A}{\sqrt{2}} \) (cf. Figure 2-10). This implies that the bcc cell has to be transformed in a tetragonal manner, which means that the c-axis has to be lowered by 20% and the a-axis has to be elongated by 12%. The relation between a and c in martensite \( \left( \frac{c}{a} \right) \) depends on the C concentration given in the material.

![Figure 2-10: Sketch of the transformation of fcc to bcc following the bain modell. a) shows two fcc cells with a virtual bcc cell, b) shows the virtual bcc cell and d) is the martensite cell. ([34] p. 159; reprinted from Werkstoffkunde Stahl für Studium und Praxis with permission from Wissenschaftsverlag Mainz)](image)

A common model for the transformation is the “Bain-Modell” forwarded by E. C. Bain, which successfully describes the shearing of the crystal lattice. From experiments it is found that martensite and the original austenite have an invariant habit plane. Taking this into account, one realizes that the Bain transformation describes successfully the lattice deformations but delivers the wrong shape of the crystal. By twinning or slipping, it is possible to accommodate the shearing of the Bain-transformation and to get the right shape of the crystal (cf. Figure 2-11).
Figure 2-11: Types of transformations which accommodate the bain-transformation. In From a) to b) it is shown how the shape of a crystal is changed by shear during a martensitic transformation. The shape change can be accommodated by shear c) or twinning d) ([38] p. 418).

In dependence of the C and substitutional element content of the alloy, there are different orientation relations between the austenite and martensite lattices. The two most well-known are summarized in the following table.

<table>
<thead>
<tr>
<th>Name</th>
<th>Orientation relation</th>
<th>Habit plane</th>
<th>Orientation variants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kurdjomov-Sachs relation</td>
<td>{111}_A</td>
<td></td>
<td>(110)_M</td>
</tr>
<tr>
<td></td>
<td>(110)_A</td>
<td></td>
<td>(111)_M</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>- 1.4 wt. % C)</td>
</tr>
<tr>
<td>Nishiyama-Wasserman relation</td>
<td>{111}_A</td>
<td></td>
<td>(110)_M</td>
</tr>
<tr>
<td></td>
<td>(112)_A</td>
<td></td>
<td>(011)_M</td>
</tr>
<tr>
<td>Greninger-Troiano [40]</td>
<td>{111}_A</td>
<td></td>
<td>about 0.2° from (110)_M</td>
</tr>
<tr>
<td></td>
<td>(101̅)_A</td>
<td></td>
<td>about 2.7° from (011)_M</td>
</tr>
<tr>
<td></td>
<td></td>
<td>towards (111)_M</td>
<td></td>
</tr>
</tbody>
</table>

Table 2: Crystallographic orientation relation during the formation of martensite ([34] p. 161)

The C concentration in the former austenite influences not only the orientation relation between austenite and martensite but also the temperature at which the transformation starts (M_s). It can be calculated using the following empirical equation.

\[
M_s(°C) = 550 - 350(\%C) - 40(\%Mn) - 35(\%V) - 20(\%Cr) - 17(\%Ni) - 10(\%Cu) - 20(\%Mo) - 8(\%W) + 15(\%Co) + 30(\%Al)
\]

Unfortunately, it is not possible to calculate the martensite finish temperature (M_f) using an equation which exclusively relies on the composition of the alloying elements (For a more genuine description see [34, 41]).
2.4.4. Different types of ferrite

Even though, the phase ferrite is quite well defined (BCC crystal structure in iron), there exist different types of ferrite, which can be distinguished by their growth regime, shape and the accompanying phases. Two different growth regimes are known, the reconstructive and the displacive growth of ferrite. According to Bhadeshia, Widmanstätten ferrite [42], bainitic ferrite (cf. Chapter 2.4.2), acicular ferrite [43, 44] and martensite (cf. Chapter 2.4.3) belong to the displacive phase transformations [45]. As diffusive phase transformations he counts allotriomorphic ferrite [46], idiomorphic ferrite, massive ferrite and pearlite (cf. Chapter 2.4.1.)

Allotriomorphic ferrite as well as idiomorphic ferrite are both formed reconstructively, which means that during the phase transformation the parent lattice atoms are able to diffuse and to form a new lattice [47]. Idiomorphic ferrite is known to nucleate at inclusions within austenite grains, whereas allotriomorphic ferrite forms itself at the austenite grain boundaries [48, 49]. Both types of ferrite have polygonal shaped grains.

As already mentioned the growth regime of Widmanstätten ferrite has a displacive character and can occur at temperatures close to the paraequilibrium \((\alpha + \gamma)/\gamma\) phase boundary [45]. The grains are lath like shaped [42] and according to Bhadeshia [50] the growth rate is \(C\) diffusion controlled, which means that during the growth of Widmanstätten ferrite the bcc lattice is not supersaturated with \(C\). In contrast to the growth of Widmanstätten ferrite the nucleus of Widmanstätten ferrite growth reconstructively [45].

Acicular ferrite as well belongs to the displacive phase transformations. It consists of fine-grained laths, which grow within the prior austenite grain [51]. According to Bhadeshia et al. acicular ferrite can be named as intergranularly nucleated bainite, which grows for larger austenite grain sizes if enough non-metallic inclusions are present [52]. G. Thewlis define acicular ferrite as a mixture of different intergranular formed ferrite types, which could have been grown reconstructively or displacively [53]. According to him, acicular ferrite is a consequence of the hard impingements of different transformation products. Steel welds are known to contain acicular ferrite, since the weld metal inclusions provide a high number of nucleation sites [44].

Bhadeshia reported that in general, a massive transformation is defined as a diffusional phase transformation, in which the parent and the product phase have the same composition [54]. In the same paper he presents many studies which show that in Fe and its alloys a massive transformation occurs only in very low \(C\) steels.
2.5. **X-rays**

Even though modern X-ray spectral analysis software is a great help for analysis and delivers reliable results for standard conditions, one has to be aware of its limits. This introduction will help to develop a deeper understanding on the reliability of X-ray analysis in the context of the present work.

X-rays are electromagnetic radiation with a wavelength between 0.003 and 3 nm ([55] p. 817). They were discovered in 1896 by Wilhelm Conrad Röntgen [56]. There are two kinds of X-ray radiation which differ in their origin, the bremsstrahlung and the characteristic X-rays. In X-ray spectral analysis both kinds are found and have to be taken into account.

2.5.1. **Bremsstrahlung**

This section is mainly a summary of Chapter 7.5.1 of [57]. Bremsstrahlung is created, if an electron hits material and is deflected by the positive nucleus of an atom. During the process of deflection the electron loses energy in the form of photons, which is called bremsstrahlung. The maximum total energy which can be transferred from the electron to the photon corresponds to the energy of the primary electrons. Its wavelength can be calculated by the following equation:

\[
\lambda_M = \frac{h \cdot c}{e \cdot U}
\]

(2.10)

Here, \( \lambda_M \) is the maximum wavelength of the bremsstrahlung photon, \( h \) is the Planck's constant, \( c \) is the speed of light, \( e \) is the charge of an electron and \( U \) its accelerating voltage.

In Figure 2-12, one can see specific bremsstrahlung spectra created in tungsten by electrons. For every accelerating voltage there is a wavelength with a maximal intensity, which indicates the most likely energy loss of the electron.
Figure 2-12: Intensity of bremsstrahlung in dependence of the wavelength created in tungsten for different electron energies ([57] p. 255)

2.5.2. Characteristic X-rays

This section is mainly a summary of the Chapter 4.2. from [58]. Characteristic X-rays are created when the incident electrons have sufficient kinetic energy to ionize electrons of an inner shell. The missing inner shell electron creates a higher energy level of the excited atom. To minimize its energy an electron of an outer shell fills the vacancy in the inner shell. As a result the energy difference between both electron shells will be emitted in the form of an Auger electron or a photon, which is called the characteristic X-ray. To calculate its wavelength, one needs to take into account the relation between the energy and wavelength for photons,

$$E_D = h \cdot v = h \cdot \frac{c}{\lambda_X} \rightarrow \lambda_X = \frac{h \cdot c}{E_D}$$  \hspace{1cm} (2.11)

Here, $E_D$ is the energy between the two electron shells, $h$ is the Planck’s constant, $c$ is the speed of light and $\lambda_X$ is the wavelength of the characteristic X-ray photon ([57] p.89). As it can be derived from this formula, bigger energy differences lead to shorter wavelengths of the photon. The naming convention of the different transitions between the energy shells is shown in Figure 2-13. This will now be explained in more detail for the K- and the L-line. The electron shell closest to the nucleus of an atom is called the K-shell. The binding energy for electrons of the K shell is higher compared to the outer shells. If an electron of a specific shell gets ionized, the produced characteristic X-rays will be named according to the respective shell. For further clarification, the X-rays obtain a suffix indicating the original shell of the electron filling the vacancy. $K_{\alpha_1}$ means that the electron responsible for the X-ray is coming from the most outlying L-subshell and fills a vacancy in the K-shell. For the X-rays created by
electrons transferred to the L-shell, the naming convention has to be expanded. This is necessary because the L-shell has 3 different subshells. LIIB1 describes an X-ray quant caused by an electron coming from the β1-shell down to the L1 shell.

![Diagram of electron transitions](image)

**Figure 2-13: The possible electron transitions for the K, L, and M line ([58] p. 56)**

Which characteristic X-ray lines are present for a given element depends on its atomic number. Elements with a higher atomic number have more electrons, which are distributed on more shells. C for example only has a K-line while Fe also has L-lines. A table containing all possible characteristic X-rays can be found in [59] and many other sources.

The probability of creating a specific X-ray strongly depends on the ionization cross section \( \sigma_I \) of the shell. The higher the cross section, the higher is the chance for an electron to create characteristic X-rays. \( \sigma_I \) itself is influenced by the overvoltage. The overvoltage is defined as \( \frac{E_0}{E_c} \), whereby \( E_0 \) is the energy of the incoming electrons and \( E_c \) is the ionization energy for a specific shell. At least an overvoltage of 1 is necessary to create characteristic X-rays because otherwise the free electron does not have enough energy to ionize an inner shell electron. The dependence between the overvoltage and \( \sigma_I \) in general is plotted in Figure 2-14.
The maximum of $\sigma_I$ lies at an overvoltage of 3 and slowly decreases afterwards. Since $E_c$ depends on the analysed element and the chosen characteristic line, the overvoltage is not the same for all elements for a given accelerating voltage. This has to be considered when choosing the measurement conditions.

When incoming electrons ionize a bounded electron of a specific element, not only X-rays, but also Auger electrons can be generated. This implies that instead of transferring the released energy to a photon the energy is transferred to another electron lying at an outer shell which then may leave the atom. The so-released electrons are called Auger electrons. Which of both processes takes place mainly depends on the atomic number ($Z$) of the ionized element.

According to Williamsen et al. ([58] p. 59), the chance that during the ionization of an inner-shell electron an X-ray photon is produced ($\omega$), can be described with

$$\omega = \frac{Z^4}{a + Z^4},$$  

(2.12)

where $a$ is a constant without units, which varies for different electron shells. For the K-shell the value is $\sim 10^6$. The value of $\omega$ for the K-shell for different elements is plotted in Figure 2-15. It can be seen, that for light elements like C the generation of Characteristic X-rays is much more unlikely in comparison to the generation of X-rays from atoms with higher atomic numbers like Fe.
2.5.3. **Spatial resolution of X-ray measurements in SEM**

The physical principles responsible for the spatial resolution of energy-dispersive X-ray spectroscopy (EDX) and wavelength-dispersive X-ray spectroscopy (WDX) in SEM are the energy loss of electrons traveling through matter\(^1\) and the energy loss of X-rays\(^2\), whereby the energy loss of electrons is of greater importance. If electrons are travelling through a layer of thickness \(z\), its energy loss can be approximated as follows ([60] p.155):

\[
\frac{dE}{dpz} = -\frac{b}{2E} \quad \text{(Bethe range)} \tag{2.13}
\]

\(E\) is the energy of the electrons, \(\rho\) is the density of the material and \(b\) is a constant with

\[
b = 3 \cdot 10^{11} \frac{eV^2 cm^2}{g} \tag{2.14}
\]

A simple approach to calculate the spatial resolution of X-ray analysis in SEM has been proposed by Eggert et al. ([60] p. 22):

\[
Z_m = 0.033 \cdot \frac{(E_0^2 - E_c^2)}{\rho} \tag{2.15}
\]

Here, \(E_c\) is the energy of the Characteristic X-ray line, \(E_0\) the energy of the electron beam, \(\rho\) is the density of the material and \(Z_m\) is the lateral resolution in \(\mu\)m. A detailed derivation of this formula can be found in ([60] p. 155). The assumptions made for the equation are:

- The lateral resolution is the same as the resolution in depth.

---

\(^1\) All phenomena responsible for the energy loss of electrons interacting with matter are described in [58] chapter 4

\(^2\) A detailed description of the interaction of x-rays with matter can be found in the book Experimentalphysik 3 written by Demtröder ([57] p. 256 – 251).
2. Theoretical background

- The point where no characteristic X-rays are generated anymore is defined by the point at which the electrons do not have sufficient energy to ionize an atom.
- Absorption of X-rays in matter does not play a big role.
- Electrons only move towards one direction.

2.5.3.1. Simulation of the spatial resolution of X-ray measurements in SEM

For a more detailed analysis of the spatial resolution of X-ray measurements, including the effect of x-ray absorption, the Monte Carlo Simulation Program CASINO [61] can be used. This program simulates the interaction of electrons with matter and helps to analyze the generated signals including characteristic X-rays in different ways. Pinard et al. for instance employed the program to calculate the depth resolution for C during a microprobe measurement [62]. They defined the depth resolution as the depth down to which 90 % of the C X-ray signal is emitted. In the study at hand, the interaction of an electron beam with the analysed material has been simulated using CASINO (Version 2.42). The simulated beam diameter was set to 5 nm. The accelerating voltage has been varied between 5 and 15 kV. The specimen was tilted to 0°. The composition used for the simulation is presented in Table 3 on page 55.

Figure 2-16, the energy of the electrons in the steel is plotted in dependence on position. The accelerating voltage was set to 15 kV. The different coloured lines indicate the kinetic energy of the electrons at the given positions. Knowing the ionization energy of a specific line allows one to roughly estimate the lateral resolution of the X-ray signal. It is also possible to plot the intensity of the generated X-rays either in dependence of the depth of the material or in dependence of the radial distance to the electron beam.
Figure 2-16: Energy of the electrons in % of the starting energy in dependence of the position. The simulation was performed with CASINO (Version 2.42) at 15 kV.

Figure 2-17: Depth resolution of the K-alpha line of Mn in the DP-steel calculated at 15 kV with CASINO (Version 2.42).

Figure 2-17-a) illustrates the calculated intensity profiles for Mn in the DP-steel. The black line shows the intensity of K-alpha X-rays in dependence of the depth. The red line shows how much of the signal is actually leaving the material. One can clearly see that nearly no absorption takes place in the case of the Mn-K-alpha line. In Figure 2-17-b) the integrated intensity fraction of the total intensity is plotted in dependence of the depth. The black cross indicates the depth from which 90 % of the signal is emitted.
Figure 2-18 Depth resolution of the K-alpha line of Mn in DP-steel calculated at 15 kV with CASINO (Version 2.42).

For the C K-α line, absorption plays a much bigger role. As shown in Figure 2-18-a) most of the Characteristic C X-rays are absorbed in the specimen and do not leave it. The difference in generated X-rays and measured X-rays is even more visible in Figure 2-18-b. The depth where one finds 90% of the generated X-rays is 466 nm. However, once absorption has been taken into account the depth reduces to 148 nm. Comparing the simulations of the K-alpha line of Mn and C shows that the C signal is generated in a greater depth compared to Mn. Yet, once absorption has been taken into account; the depth resolution of C is more than twice as good as the Mn resolution. In order to reveal the influence of the accelerating voltage, several simulations with varying accelerating voltage have been performed. In Figure 2-19, the depth resolution for Mn and C is plotted for different accelerating voltages. The plotted depth values are again the depths from which 90 % of the emitted signal including absorption is coming from. It appears evident that for the Mn K-alpha line the depth resolution depends much more on the accelerating voltage compared to the C-alpha line. This is due to the stronger dependence of the depth resolution on the effect of absorption of soft X-rays. Almost every K-alpha X-ray of C is absorbed if it is created deeper than 150 nm.
Figure 2-19: Comparison of the depth resolution for the K-alpha line of Mn and C in the DP-steel for different accelerating voltages calculated with CASINO (Version 2.42).

Figure 2-20: Result of the simulated linescan for C with CASINO (Version 2.42). The used accelerating voltage is 10 kV and the measured C line is the K-alpha line. The grey area shows the length in which the C signal rises from 10 % to 90 %. The spot size of the beam is 5 nm.

In order to measure the lateral resolution, a procedure similar to the one described by Pinard et al. was used [62]. A linescan over a boundary, separating two areas which differ in the content of Mn and C, was simulated using Casino 2.42. The step size was 25 nm. The boundary itself is orientated perpendicular to the surface and has no thickness itself. The scan is started 1000 nm away from the boundary and stops 1000 nm after it. On the left side
of the boundary the material had a C content of 0.0138 Wt. % and a Mn content of 1.82 Wt. %.
On the right side of the boundary the material had a C concentration of 0.138 Wt. % and a
Mn content of 6 Wt. %. The Fe content is on both sides of the boundary balanced and the
other substitutional elements have the same concentration levels as shown in Table 3 on
page 55. The X-ray intensity was normalized in a way that 0 % is the element concentration
in the lower concentrated region and 100 % is the concentration in the higher concentration
region. The lateral resolution was determined by measuring the length on which the intensity
of the characteristic X-ray line of Mn or C dropped from 90 % to 10 %. A typical result of such
a simulation can be seen in Figure 2-20. Here the linescan was simulated with an accelerating
voltage of 10 kV. The lateral resolution for C lies here at 230 nm, which is much higher than
the depth resolution of C at 10 kV, which lies at 130 nm. For a comparison of the lateral
resolution calculated with Monte Carlo simulations and the resolution derived by
Equation (2.15), Figure 2-21 was derived. In order to calculate the lateral resolution with
Equation (2.15), the density of Fe (7,874 g/cm²) was used. For C as well as for Mn the Monte
Carlo simulations deliver a smaller lateral resolution than the equation. It appears evident
that for higher accelerating voltages the difference between the values calculated with the
equation and the ones calculated with Monte Carlo simulations increases. Equation (2.15) can
only be used to obtain a safe upper limit for the lateral resolution. For a detailed analysis,
Monte Carlo simulations are needed.

Figure 2-21: Comparison of the lateral resolution of Mn and C determined with Monte Carlo
simulations (CASINO (Version 2.42)) and equation (2.15). For (2.15) the density of Fe was
assumed.
2.5.4. The ZAF-correction model

This section provides a summary of pages 411-425 of Reimer’s text book “Scanning Electron Microscopy - Physics of image formation and microanalysis” [63]. In order to perform a quantification of an X-ray spectrum, a correction model has to be used. When only comparing the count rates for every element with each other in the material, it is not possible to calculate the concentration levels. This is due to several physical effects which weaken or enhance different characteristic lines differently. The ZAF-correction model takes these physical effects into account. The measured counts of a characteristic line $i$ ($N_{ch}^i$) can be described using the following equation:

$$N_{ch}^i = \frac{d\Omega}{4\pi} i_0 t \varepsilon_i \omega_i q_i c_i (ZAF)^{ch}_i,$$

(2.16)

where $\frac{d\Omega}{4\pi}$ is the solid angle of the detector, $i_0 t$ is the total amount of electrons hitting the material, $\varepsilon_i$ is the efficiency of the detector for the specific line, $\omega_i$ is the fluorescence yield for the characteristic X-rays in general, $q_i$ describes probability that the Characteristic X-ray $i$ is emitted and $c_i$ is the concentration of the analyzed element in the material. The term $(ZAF)^{ch}_i$ describes the correction applied for the atomic number ($Z$), the absorption correction ($A$) and the fluorescence correction ($F$). The detailed calculation of this term is nowadays performed by X-ray analysis programs. The Z-correction takes two different issues into account, the backscattering factor and the amount of created electron vacancies in dependence on the atomic number. A material with a high density (high average atomic number) causes a more rapid slowing-down of electrons compared to materials with low atomic numbers, which means that the electrons travel shorter distances and loose faster the kinetic energy. This implies that the electrons have a lower probability to create characteristic X-rays, since the electrons can only create vacancies as long as their kinetic energy is high enough. The backscatter factor takes into account that electrons can leave the material before they lose their energy which is necessary to create vacancies. The A-correction considers the absorption of X-rays in a material. In general, high energy X-rays get less absorbed than low energy ones. The absorption is also different for different specimen geometries like tilted specimens. It can be only calculated for known geometries. The F-correction deals with the influence of secondary fluorescence. For example, it may be possible that high energy X-rays can create low energy X-rays and also bremsstrahlung can create characteristic X-rays. All three factors depend on the composition of the material. They therefore have to be calculated iteratively, starting with a first guess for composition and refining the composition in each iteration step. Moreover, one has to be aware that a correct calculation is only possible if the measurement is conducted under known conditions. A flat polished surface and bulk material are necessary for a successful analysis.
2.5.5. The peak to background method

The peak to background (P/B-ZAF) method is a relatively new correction algorithm which uses the bremsstrahlung for an easier quantification of the concentration levels in place. For a given energy interval the bremsstrahlung can be calculated as follows:

\[ N_{i}^{br} = \frac{d\Omega}{4\pi} i_{0} t e_{i} c_{i} (ZAF)^{br}_{i} \]  

(2.17)

Dividing the intensity of specific characteristic X-ray line by the bremsstrahlung of the same position leads to:

\[ \frac{N_{i}^{ch}}{N_{i}^{br}} = \frac{\omega_{i} q_{i} c_{i} (ZAF)^{ch}_{i}}{(ZAF)^{br}_{i}} \]  

(2.18)

The A-correction of bremsstrahlung and characteristic X-rays is nearly 1. Since the bremsstrahlung and the Characteristic X-rays are absorbed nearly in the same way in the material. This implies that the absorption corrections do not have to be taken into account anymore, which allows one to analyse unknown specimen geometries as well as rough surfaces. Moreover, it is not necessary to take the geometry of the detector and the intensity of the beam into account. The limit of this method is the analysis of low energy lines. In general, it can be said that elements with Z > 11 can be quantified without any problems using the peak to background method.
2.6. **Electron Backscatter Diffraction (EBSD)**

Electron Backscatter Diffraction is a technique used in SEM to obtain quantitative crystallographic and microstructural information of crystalline materials. For instance, grain size, grain orientation, texture and phase type can be measured routinely with this technique ([64] p. 41). Over the last 20 years the method became increasingly popular in the scientific community, which is indicated by the increasing number of EBSD related publications ([65] p. 17). The entire procedure is based on the automatic analysis of backscatter Kikuchi patterns formed in SEM [66]. The spatial resolution of EBSD at 15 kV on Fe is 90 nm in perpendicular and 30 nm in parallel direction (70° tilted specimen) [66]. The following chapter will provide a brief introduction to the formation process of Kikuchi patterns in SEM.

Figure 2-22: Number of EBSD-related papers published per year since 1990. ISI Web of Knowledge was used by the original author as a source for the number of publications. Higher amount of papers can be found in years of ICOTOM conference ([65] p. 17).

2.6.1. **The formation of Kikuchi (EBSD) patterns in SEM**

There are different ways of how the formation of EBSD patterns can be described. The phenomenological description, which will be discussed here, is divided into two parts. At first the electron beam produced by the SEM is scattered incoherently somewhere in the material and the electrons travel in all directions. This process can be described as the formation of a divergent electron source in the material. Secondly, the electrons coming from this source undergo an elastic and coherent scattering. At all angles, , fulfilling Bragg’s law, high electron intensity is found, the locus of which corresponds to pairs of cones (Kikuchi cones) with an opening angle of 180° -20. The cone axis is perpendicular to the plane which causes the diffraction. The geometrical relations can be seen in Figure 2-23. The interaction between the cones and the detector phosphor screen is tangential to the propagation sphere and nearly forms parallel lines (Kikuchi lines). The distance between the lines is a characteristic feature
of the lattice plane spacing and the position of the centre line of the Kikuchi band determines the position of the diffracting lattice plane. The intensity distribution in a Kikuchi band between two Kikuchi lines cannot be explained phenomenological. A theory which allows to explain the contrast of a Kikuchi band is the Bloch wave theory [63]. Kikuchi patterns are unique for every crystal structure and orientation and are used for the analysis of the crystal type and orientation.

Figure 2-23: Sketch of the geometrical relations during the formation of EBSD patterns. The incoherent scattered electrons in the material describe an ellipse. The highest intensity is approximately found for $\beta = \alpha$. [66]
3. Experimental methods

As already discussed in the introduction, the investigations have been performed on two different steels. The first one is a commercially-processed dual phase steel and the second one is hot rolled material which is processed in the institute’s laboratory. The commercially-processed dual phase steel is provided in two variants formed out of a bainite plus martensite microstructure (B+M) and material in which the microstructure showed a perlite plus ferrite structure (P+F) after cold rolling. The material, processed in the institute (in-lab-processed material) is provided in the form of 3.7 mm thick plates. Again both variants, P+F and B+M, are present. In the following, all methods which were used to analyse the different types of steel will be presented.

3.1. Dilatometer experiments

For the dilatometer experiments the material is cut into cylinders with a diameter of 4 mm and a length of 9 mm. The rolling direction is perpendicular to the front surface (cf. Figure 3-1). Since the 4 mm cylinders were cut out of material with only 3.7 mm thickness the cylinders are slightly flattened. A dilatometer DIL 805A/D produced by TA Instruments [67] was used. It is equipped with an induction heating system, which guarantees fast heating rates. To avoid oxidation of the specimens, the experiments can be performed under vacuum or under inert gas atmosphere. For cooling down, different gasses can be inserted into the measurement chamber. Besides the temperature (± 0.05°C), which is measured using a thermocouple, the time and the length change of the specimen (± 50 nm) can be measured as well. A typical set of curves used for the analysis of the dilatometer experiments can be found in Figure 3-2. Figure 3-2-a) shows the temperature of the specimen in dependence of the time. Comparing this curve with the applied temperature regime allows one to judge whether temperature control was accurate or not. In Figure 3-2-b) the length change is plotted in dependence of the temperature. A nonlinear relation between temperature and length change can indicate a phase transformation, if the two phases have a different density. The third curve (cf. Figure 3-2-c) shows the length change in dependence of the time. Analysing this plot in conjunction with Figure 3-2-b allows t see when a phase transformation during an isothermal heat treatment is completed.

Figure 3-1: Sketched front view of the dilatometer specimen
Experimental methods

3.2. Hardness measurements

3.2.1. The Vickers hardness

For hardness measurements, the specimens are ground, polished until 3 µm diamond suspension and finally polished with Oxide Polishing Suspension (OPS). All hardness values were measured with a microindentation hardness testing system (LM 100 AT) supplied by the company Leco. The used indenter has the shape of a right pyramid with a square base. During the measurement procedure the indenter is loaded with a specific weight and afterwards the diameter of the indentation is measured. The Vickers hardness (HV) is calculated as follows:

\[ HV = 1.854 \cdot \frac{F}{d^2}. \]

Here, \( F \) is the applied force and \( d \) is the diameter of the indentation. For every specimen 10 measurements have been performed and the standard deviation is set as the error. A detailed introduction to the measurement procedure itself can be found in ([68] p. 315).
3.3. **Optical microscopy (OM) for microstructure characterization**

Optical microscopy is used to get an overview on the microstructure of the examined material at different points of the production process. The specimen preparation process is the same as that for the hardness measurements with one exception. To enhance the contrast of the images, different etching solutions are used. The most common one is Nital, which consists of ethanol and nitric acid ([69] p.3913). In the study at hand the used solution had 1 % vol. nitric acid. All OM-images were taken in longitudinal section.

3.4. **SEM based techniques for microstructure characterization**

In materials science the SEM is one of the most frequently used tools, since it offers a great variety of different analytical techniques. In contrast to a transmission electron microscope, it generates an image of the sample by scanning a focused electron beam over the surface of a specimen (cf. Figure 3-3). The magnification can be calculated by dividing the size of the displayed area with the size of the scanned area (cf. Figure 3-3). The interaction of the electron beam with the material can be analysed using different detectors. The standard detector for image formation in SEM is the secondary electron detector, which delivers topological information of the specimen by collecting the low energy secondary electrons ($< 50$ eV). Two different microscopes were used for the performed measurements. The first one is a JEOL 6500 F SEM with a Shottky field-emission gun (FEG-SEM). This SEM is equipped with an EBSD system of EDAX/TSL and a digiview EBSD camera. The EDX detector is a silicon drift detector from EDAX as well. The second microscope is also equipped with a field-emission gun. It is a Zeiss-Crossbeam XB 1540 equipped with an EBSD and EDX system of EDAX/TSL as well. A specific feature of this instrument is the scanning transmission detector (SEM-STEM) mounted to the system. It allows analysis of electron transparent samples in SEM.
3.4.1. Preparation of bulk specimens

There are two different ways, how the specimens were prepared for the SEM measurements. For EBSD all specimens were grinded, polished until 3 µm and polished with Oxide polishing suspension for 10 minutes. After this time the surface was flat and free of scratches as it is needed to obtain good EBSD patterns. For microstructural investigations with secondary electrons, the specimens were etched using Nital until the different phases could be distinguished easily. For both methods the preparation has been performed in such a way that the rolling direction is perpendicular to the front surface (cf. Figure 3-1).

3.4.2. Preparation of extraction replicas

Extraction replicas were prepared to carry out a detailed analysis of the carbides in the steel. The procedure is similar to the method described by David B. Williams et al. ([58]p. 184). The specimens were polished the same way, as they were for EBSD. Afterwards the specimens were etched with a 2 pct. Nital solution. In order to achieve comparability for the results, all specimens were etched during the same lab session and for the same time (30 s). After this, the specimens were C coated by evaporation of C followed by a deposition of ethyl acetate on the C layer. After drying, the lack was divided into small pieces using a scalpel. In order to ease removal of the extraction replicas from the surface, the specimens were deposited in distilled water and nitricic acid was put on the sample drop by drop until the extraction replica lost the contact to the surface. By using tweezers, the extraction replicas were taken out of the water and deposited on TEM-grids and subsequently dried.
3.4.3. EBSD on bulk specimens

There are two different kinds of EBSD measurements, which have been performed on the bulk material, the standard single-map EBSD measurements and large area multi-map EBSD scans.

3.4.3.1. Standard EBSD measurement results

All standard measurements were performed in a JEOL 6500 F SEM with specimens tilted to 70 °. The used data collection software is OIM data collection (version 6.2) distributed by EDAX/TSL. It analyses the EBSD patterns measured with a Digiview camera by applying a Hough transformation on the patterns [71]. This procedure allows the software to transform the Kikuchi bands into so-called Hough peaks, whereby its height is determined by the contrast of the bands. The middle of such a peak approximately corresponds to the centre line of a Kikuchi band and can be detected by the software. The results are compared to a database of known crystal structures and the most reliable solution according to phase and orientation is selected [72]. The expected crystal structures have to be chosen before the measurement, as the step size and the size of the scanned area. To improve the quality of the measured patterns, two different backgrounds can be subtracted from the raw patterns. For the standard static background subtraction the beam is scanned over a large area with a high scanning speed and the EBSD camera is illuminated for a specific time. This delivers an image of homogeneous illumination of the camera which is subtracted from the measured pattern images. The second method is called dynamic background correction. During this procedure the background is calculated directly from the measured pattern by blurring the pattern with a large radius Gaussian convolution mask [73]. Besides phase and orientation of each measured point, the software saves the image quality (IQ) of the patterns and the confidence index (CI). The IQ describes the quality of a pattern. It is defined by the average height of the Hough peaks [74]. The CI refers to the reliability of the found solution. It is scaled between 0 and 1. If for fcc materials at least 6 Kikuchi bands are identified, a CI greater 0.1 means that 95 % of the patterns are indexed correctly [75]. For all analyses performed with EBSD, usually only the points with a CI greater than 0.1 were used. In those cases where all points with a CI < 0.1 were taken into account, it will be explicitly mentioned. During the majority of the measurements the camera was capable of a collection rate of about 70 frames per second (70 fps).

The measured EBSD maps were analysed with the software package OIM Analysis (version 6.2). To measure the grain size of the different phases, the software has to translate the measured orientations into grains. Therefore, it analyses the orientation of a point (point x) and its neighbouring points. If the orientation of point x and its neighbouring points are misoriented by less than a predefined threshold value, they are counted to one grain. The
value for the misorientation which is accepted by the program can be defined. It is also possible to define a minimum size for a grain in the software, which means that only grains with a certain size are included into statistics. In the present study, all neighbouring points with a misorientation less than 5° are counted as one grain and the minimum grain size is 2 points. As a clean-up procedure for all measurements, CI standardization was used. This procedure changes the CI values of all measurement points belonging to one grain to the highest CI value of all points belonging to one grain.

The microstructure analysed with EBSD after the entire heat treatment consists mainly of ferrite, martensite and austenite. Since ferrite and austenite differ in their crystal structure, it is straightforward to distinguish both with EBSD. Martensite and ferrite have the same crystal structure. The method used to distinguish both phases is similar to the one described by Pinard et al. in detail [62]. It is known that martensite has a higher defect density compared to ferrite, which leads to a lower IQ. This is due to the lower pattern quality of the patterns obtained in martensite [74, 76]. To exclude the effect of grain boundaries, which have a low IQ as well, the grain average IQ is used. A typical plot of the distribution of the grain average IQ is shown in Figure 3-4. One can see that the differentiation between ferrite and martensite is not always straightforward, since the boundary between the IQ region belonging to the martensite and the IQ related to the ferrite is not very sharp. This is due to the fact that some bcc grains are quite small and have a low IQ but not such a low grain average IQ as other martensite grains. Therefore it was not possible to tell whether they were martensite or ferrite. In such cases, an upper and a lower value for the martensite content were determined. The upper value included all martensite grains including the unsecure ones. The lower value selected only the bcc grains which were clearly martensite. Both values were selected by checking visually in the EBSD map whether the right bcc grains were selected or not. The average of both values was set as the martensite content. As an error for this procedure both values have been subtracted from each other and the precise half of this value was set as an error. Additionally all points with a CI < 0.1 were counted to martensite.
3.4.3.2. **Calculation of the geometrically necessary dislocation density**

In literature it is reported that strain hardening in ferrite is mainly caused by immobile dislocations, whereby two different types of immobile dislocations exist, namely the statistically stored dislocations (SSDs) \([77, 78]\) and the geometrically necessary dislocations (GNDs). SSDs are dislocations which are generated due to the random interaction of dislocations during plastic straining \([79]\). This type of dislocations accumulates due to entanglement with each other. GNDs in contrast, are dislocations which are needed to describe the heterogeneity of plastic deformation which creates curvature of the crystal lattice \([78, 80]\). The dislocation density \(\rho_{\text{GND}}\) needed to accomplish the curvature \(K\) is defined by

\[
\rho_{\text{GND}} = \frac{K}{b}
\]  

(3.1)

whereby \(b\) is the Burgers vector. Both types of dislocations cause strain hardening, since both types of immobile dislocations prevent the movement of other dislocations. According to the work of Demir et al \([79]\), which is based on the work of Kocks \([77]\), the relation between the yield strength of a material and the density of GNDs and SSDs can be described as follows.
\[ \tau^\alpha = c G b \sqrt{\rho_{GND}^2 + \rho_{SSD}^2}. \]

Here, \( c \) is a geometrical constant between 0.5 and 1, \( G \) is the shear modulus of the material and \( \tau^\alpha \) is the critical resolved shear stress on the slip system \( \alpha \). This equation is based on a homogenization assumption, which means it is assumed that the dislocations are distributed homogeneously in the material.

For the purpose of determining the geometrically necessary dislocations (GND) densities in a material, kernel average misorientation (KAM) measurements are of great worth. In OIM data collection (version 6.2) the KAM value is calculated from EBSD maps as the average misorientation angle between a centre pixel and all its neighbours, thereby excluding pairs with larger misorientations than 4°. It is possible to define in the software the size of the kernel and the maximum misorientation. KAM values obtained from different measurements are only comparable, when the used step size is the same.

There exist several ways, how the GND density can be calculated directly from the KAM values. In a study by Calcagnotto et al. [81] a method was shown which bases on the work of Kubin and Mortensen [82]. Under the assumption that a series of twist subgrain boundaries in a cylinder contains two perpendicular arrays of screw dislocations, the GND density can be calculated as follows:

\[ \rho_{GND} = \frac{2\theta}{ub} \]  \quad (3.3)

where \( \theta \) is the misorientation angle, \( u \) is the measurement length, which will be defined in the following, and \( b \) is the magnitude of the Burgers vector. For an approximation, the KAM can be used as the misorientation angle. For an EBSD measurement the unit length \( (u) \) depends on the step size \( (a) \) and the n-th KAM values as follows:

\[ u = a \cdot n. \]  \quad (3.4)

Hence most of the examined material is bcc, the length of the Burgers vector can be calculated to \( b = \frac{d_{bcc}}{2} \sqrt{3} \), with \( d_{bcc} \) being the lattice constant of the unit cell of bcc-iron.

For all GND mappings the 2nd neighbour KAM was used. The average GND densities in ferrite were calculated as described in Chapter 8.1.

3.4.3.3. Large area EBSD measurements

The technique of large area EBSD measurements has been developed by Davut et al. [65, 83]. With applying their method, it is possible to analyse vast areas of the surface by measuring several small maps on different positions on the surface. Davut et al. compared the results obtained by a measurement with a large step size and the results of the large area technique
They found that with both techniques it is possible to analyse a huge amount of grains, which increases the reliability of texture and phase fraction analysis, but with the large area technique it is additionally possible to...

- ...obtain information about local features in the material.
- ...apply grain based data clean-up processes such as grain CI standardization.
- ...measure grain average based properties of the material.

This was of great importance for the present study, since it allowed measuring the martensite fraction with the grain average IQ.

In Figure: 3-5, one can see a sketch of the large area EBSD technique. It shows that it is necessary to define the size of the small maps, the step size between them and the number of them. For this technique, a Zeiss-Crossbeam XB 1540-SEM equipped with an EDX silicon drift detector (Apollo XL) and an EBSD system provided by EDAX was used. This Zeiss microscope can be controlled remotely which allows one to move the stage between the single measurements. In order to keep the microscope in focus, it is focused at the end points of the complete measured area and the software, which remotely controls the microscope, calculates the focus at all small measurements by interpolation. After completing the measurement, all small maps are combined to one big map which can be analyzed using the OIM Analysis program.

![Figure: 3-5 Sketch of the working principle of the large area EBSD technique. Several small maps with a high resolution (100 nm step size) are measured at different positions ([65] p. 35).](image-url)
3.4.4. **EBSD on extraction replicas**

EBSD on extraction replicas is a technique developed to analyse the carbides in the matrix in detail in SEM. This is necessary since not all carbides can be identified performing EBSD measurements on bulk specimens. In the examined material it was not possible to reliably identify cementite in the present microstructure. This is the reason why the extracted carbides were analysed using EBSD. At first the extraction replicas were positioned on a disk capable of holding TEM-samples (cf Figure 3-6). This disk was positioned on a holder pre tilted to 54°. After inserting the holder into the microscope it was tilted by 10° in direction of the EBSD detector. The total tilt angle was then 64°. This is not the optimum EBSD position but it was sufficient to obtain EBSD patterns. The best pattern quality was obtained at 30 kV accelerating voltage. Due to the missing matrix it was not possible to apply the standard background correction method on the patterns but dynamic background correction was used instead. In Figure 3-7, 3 patterns typical for the carbides present in the matrix are shown. It was possible to identify all three of them. In order to obtain high quality patterns, the exposure time was selected much longer compared to measurements on bulk specimens. In total the exposure time was 7 times longer than the exposure time used for standard EBSD measurements. Because Ti carbonitrides showed a much stronger contrast compared to M23C6 and cementite they were used to calibrate the EBSD system for the measurements.

![Figure 3-6: Sketch of the holder used for TEM grids. a) shows the grid disk from above. b) shows the pre tilted holder from the side.](image-url)
3.4.5. EDX on extraction replicas

EDX on extraction replicas offers many advantages compared to the analysis of carbides embedded in the matrix. For small carbides it is likely that during an EDX measurement the gained signal is not only produced in the carbide but also in the matrix. During the creation of an extraction replica, only the carbides are extracted. Hence, the signal can only come from the particles itself. In the present study, measurements were performed at 0° tilt position. There are two different kinds of analyses which were performed. For an exact determination of the type of the carbide, the EDX measurements were combined with EBSD. EDX mappings were obtained in order to measure the distribution of the different particles. Both methods will be presented in the following section.

3.4.6. EDX combined with EBSD

The combination of EDX with EBSD allows one to determine the exact composition of the Fe-carbides M23C6 and cementite. To separate the Fe carbides from each other, EBSD can be used. After the identification of the carbides, the specimens are tilted back to 0° and analysed with EDX in spot mode. Since the extraction replica itself consists of dried lack, it produces a strong C signal in the EDX measurements, which has to be excluded from the measurement. It is not necessary to measure the C content in the carbides since this is a stoichiometric fixed value. In contrast, the composition of the substitutional elements varies in the carbides and has to be determined with EDX. In the present work, the used EDX software is Genesis (Version 6.2). The applied correction model is the P/B-ZAF which allows one to perform correct analysis of the spectrum of small particles (cf. p. 31). In the software, the option Expert ID had to be selected to activate this correction model. A detailed description of its principles can be found in [84, 85]. As an error of measurement the standard deviation of all performed measurements on one type of carbide has been selected.
3.4.7. **EDX mappings**

For EDX mappings another specimen holder was used. It is comparable to the one shown in Figure 3-6 b) only without using pre tilting. The used detector for obtaining micrographs is the STEM detector. The mapping itself was performed using OIM data collection, since this program, in contrast to the EDX software, can be controlled remotely. This was done in the same way as for large area EBSD scans. One disadvantage of the software is that it is not possible to save the whole spectrum for every pixel, only the total count rate of certain regions of interest can be recorded. Therefore, one is forced to select the elements of interest before the measurement. During all measurements, the counts of Fe, Mn, Cr and Ti were saved. It was distinguished between Fe carbides and Ti carbonitrides using the Mn and Ti signal. M23C6 and cementite cannot be distinguished by this technique. A typical measurement can be seen in Figure 3-8. The green regions indicate the Fe carbides and the blue signal the Ti carbonitrides. The area fraction of the Fe carbides can be calculated as follows. The pixels being Fe carbide are divided by the total amount of measured pixels. The selected step size of all mappings is 50 nm. The measurement rate was adjusted in a way that the EBSD patterns are indexed right and the EDS signal shows a good background to noise level.

![Figure 3-8: Mapping of microstructure containing Ti carbonitrides and Fe carbides.](image)
3.4.8. **Electron contrast channelling imaging (ECCI)**

ECCI is a technique, which makes the observation of individual crystal defects in SEM possible. Thereby, the technique uses the strong relation between the orientation of the crystal with respect to the incident electron beam and the intensity of the backscatter electrons (BSE) [86]. The name of the mechanism responsible for the relation between the intensity of the BSE and the orientation of the sample through the incident electrons is electron channelling mechanism. If between the incident electron beam and the crystal lattice the Bragg condition is achieved, this mechanism is at a maximum and the incident electrons are not backscattered but channelled through the material [87]. This is, however, only true as long as the crystal contains no defects. Crystal defects like dislocations distort the lattice, which leads to the fact that the incident beam and the crystal lattice do not fulfil the Bragg condition anymore and the incident electrons are not channelled but backscattered (cf. Figure 3-9). In a BSE image this leads to an image in which the grain is black and the defects are white or light grey.

![Diagram showing the working principle of ECCI](image)

**Figure 3-9:** Working principle of ECCI. The red lines indicate the incoming electron beam. On the right hand side the contrast of the BSE signal is shown in dependence on the position of the incident electron beam. A high intensity is found at the position of the dislocations. \( \theta_B \) is the Bragg angle. The image is used by courtesy of Dr. Stefan Zaefferer.

In order to determine the Bragg position needed for ECCI, Gutierrez et al. showed that EBSD can be used [88]. At first the orientation of the crystals is determined with EBSD and afterwards it is calculated [89] how the sample has to be orientated that it is in optimum contrast conditions. The depth resolution of ECCI at 30 kV is 100 nm [90].
3.5. **Microprobe measurements**

In the beginning of this chapter, the differences between a WDX and an EDX detector will be presented. This is followed by a comparison of a "normal" SEM and a microprobe. The WDX detector separates the X-ray signal by Bragg's law,

\[ n \cdot \lambda = 2d \sin(\theta) \]  

(3.5)

where \( d \) is the distance between two atomic lattice planes, \( \lambda \) is the wavelength of X-rays, \( \theta \) is the incidence angle and \( n \) is an integer. The principle design of a WDX detector is shown in Figure 3-10. The crystal is shaped in a way that it focuses the incoming X-rays of a specific wavelength directly onto the proportional counter. It is not possible to use only one crystal for all wavelengths, since the angular range of a crystal is limited to \( \theta = 15^\circ - 70^\circ \) ([63] p 397). If the aim was to obtain a larger angular range, the size of the detector and the crystal would have to be unfeasibly large. In order to analyse all characteristic X-rays, different crystals are used in a detector. The crystals differ in terms of their distance of the lattice planes, which allows the detector to measure the whole spectrum. Since it is a sequential technique, one detector can only measure the counts of one characteristic line at the same time. This is also one of the main disadvantages compared to EDX, which allows one to measure the whole spectrum at the same time. An advantage of a WDS detector is the better energy resolution (5 eV WDX, 133 eV EDX ([91] p. 249) and its greater sensitivity for low energy lines like C [62].

The used microprobe, a JXA-8100 produced by JEOL, is equipped with a tungsten filament and 4 WDX detectors. The machine has a backscatter electron (BSE) detector and a secondary electron detector (SE) for image formation. The electron source is optimized to deliver high beam currents which are stable over a long time. This makes successful overnight scans possible. C contamination during WDX measurements is a serious problem, since it lowers the reliability of C measurements. The contaminations itself are caused by hydrocarbons. In the 70s, this problem was already addressed by Eichen et al. [92]. They lowered the contamination rate significantly by mounting a cold finger, a copper plate which is cooled by liquid nitrogen, below the pole piece. This technique is available at the used microprobe and was applied during this research. In order to lower the contamination rate even more, the specimens were inserted into the Microprobe one day before the measurement. This allowed the hydrocarbons located on the surface of the specimen to evaporate.
Figure 3-10: Principle design of a WDX detector. The source of the x-rays, the crystal surface and the slit of the proportional counter lie on a Rowland circle of radius $r_f$. The lattice planes are bent to $r_d = 2r_f$ ([63] p. 397)

3.5.1. Specimen preparation
At first the specimens were prepared the same way as for EBSD. Following this, they were stored in an oven to reduce the amount of hydrocarbons on the sample surface. The temperature was set to 80 °C and the samples were stored overnight.

3.5.2. Measurement and quantification
In order to reveal the distribution of the substitutional elements and C, stage mappings were performed with the microprobe. A stage mapping is a procedure where the beam stands still and the stage below is in motion. The detectors were adjusted towards the desired wavelength and the electron beam towards the needed probe current. Figure 3-11 shows the raw data of a typical measurement obtained from the examined steels. The bright zones indicate high C content. In order to quantify the results, the measured count rate was correlated with two known concentration values. This has been done for Mn and C.

As a first standard for Mn, pure Fe was used. As a second standard the average count rate of a measurement performed on the material was chosen. It was assumed that the scanned area is large enough that the average concentration of the measured area and the average concentration of the material are the same. For C, the average count rate was used as well as one standard. However, as a second standard the average count rate of pearlite was chosen. It was assumed that the present pearlite is an eutectoid one; in this case its C concentration is
well known and lies at 0.8 wt. %. No correction models like ZAF-correction were applied to the measurement.

![Graph showing counts vs. C concentration with a range from 16 to 100 counts and an average of 55 counts. The graph illustrates a C measurement on steel with measurement conditions of 15 kV, 20 nA beam current, 250 ms dwell time, and a step size of 500 nm. Pearlite islands and small carbides are visible, indicated by the higher C count rate.]

Figure 3-11: Raw data of a C measurement on steel. The measurement conditions were 15 kV, 20 nA beam current, 250 ms dwell time and a step size of 500 nm. Pearlite islands and small carbides are visible. They are indicated by the higher C count rate.

3.6. XRD measurements

X-ray diffraction measurements (XRD) have been used to determine the average fraction of retained austenite after the completed heat treatment. The dilatometer specimens have been polished until only half of the cross section was in place (cf. Figure 3-12). The XRD system uses an X-ray generator produced by General Electric (Fairfield, Connecticut, USA). Its type designation is Seifert Type ID 3003. The detector (Meteor0D) is produced by General Electric as well. The machine focuses the beam on the sample to a point. A Rietveld analysis was applied and evaluated using the software MAUD version 2.33 [93].
3.7. TEM measurements

The transmission electron microscope (TEM) was used to obtain composition, phase type and crystallographic information of small features in the material. For image formation the scanning transmission (STEM) mode was used.

3.7.1. Preparation of TEM specimens

TEM specimens were produced by a target preparation method, using a focused ion beam (FIB) milling system (Helios NanoLab 600) from FEI. This machine is a dual beam system, equipped with an FEG electron gun and an FIB. The ion source uses gallium ions. These two columns are positioned at an angle of 38°. The stage can be tilted between -10° and 60°. If it is positioned at 0°, it is perpendicular to the electron column. If it is tilted to 52°, it is perpendicular to the ion column (cf. Figure 3-13). The eucentric height and cross-over point of the electron and ion beam lies at a working distance of 4 mm. It is equipped with a gas injection system (GIS), which can be used to deposit platinum on the surface of the specimen. For lift-out procedures, a micromanipulator is installed in the microscope. The used lift-out procedure will be explained in the following section.

- Before the specimen was inserted into the chamber, it was etched with Nital. This allows finding the region of interest (ROI) easily.
- For cutting the lamella, the stage was moved to the eucentric height and tilted to 52°.
- The ROI was coated with a layer of platinum in order to protect the microstructure from gallium ion induced damage.
- Two rectangular cuts were made with the FIB at 30 kV accelerating voltage. The size of them was 12 µm in x, 8 µm in y and 7 µm in z direction. The cuts were positioned above the region of interest (ROI) and below. The distance between both was 1.5 µm (cf. Figure 3-14).
3. Experimental methods

- A third cut was made, which had the form of an L. It was positioned on the left side of the region of interest. Its size was adjusted in a way that after the cut the lamella was free on the left side.
- The specimen was tilted back to 0° and the micromanipulator was positioned on the left side from the lamella.
- The GIS was used to fix the lamella at the micromanipulator tip using Pt-deposition.
- The last connection between the bulk material and the lamella was cut and the stage was moved down.

The lamella was positioned at the left side of a TEM copper grid at the eucentric height. Subsequently the lamella was fixed at the grid using Pt-deposition.

- The specimen was thinned at 53.2° and 50.8° from two sides using the FIB in the so-called cleaning cross section mode employing a 30 kV Ga ion beam.
- At the end, the accelerating voltage of the FIB was lowered to 5 kV and the lamella was scanned for several seconds to remove most of the Ga-induced damage.

After this procedure the specimens were ready to be inserted into the TEM.

Figure 3-13: Sketch of the geometry between the columns in the FIB. The eucentric height indicates the point where sample tilts without shifts in x- and y-direction. In the case of a FIB it is also determines the point where the electron beam and the ion beam intersect with each other.
3.7.2. Diffraction experiments in TEM

Diffraction in TEM was performed to reveal the nature of small grains in the microstructure after completed annealing. To do so, the ASTAR package, a combination of hardware and software, supplied by NanoMEGAS (Blvd Edmond Machtens 79, B-1080, Brussles, Belgium) was used [94]. This package allows one to perform orientation mapping and phase analysis in TEM-based on spot diffraction pattern analysis. During a measurement, the beam is scanned over the desired area and spot patterns are saved for every measurement point and analysed automatically by the software. To perform the analysis, the software compares the acquired spot patterns via cross-correlation with the calculated spot pattern templates [94-96]. These calculated spot pattern templates have an angular resolution of 1°, which means that every 1° a spot pattern was simulated.

3.8. Thermodynamical simulations

For the present thesis, thermodynamical simulations were performed with DICTRA and Thermo-Calc (TC). Both are distributed by the company Thermo-Calc Software (Norra Stationsgatan 93, SE-113 64, Stockholm, SWEDEN). The simulations helped to get a deeper understanding of the phase transformations occurring during the thermal processing. Thermo-Calc is capable of performing thermodynamic equilibrium calculations. For the simulation of diffusional phase transformations DICTRA was employed.

3.8.1. Calculation with TC

The used TC version was 3.01. It works with the CALPHAD (“Calculations of phase diagrams”) approach to determine equilibrium phase diagrams [97]. One of its main applications in the study at hand was the calculation of 2 dimensional phase diagrams. Using those, it was possible to check whether the applied heat treatment was carried out at an appropriate temperature. In the present study, the calculated phase diagrams show most of the times the influence of C concentration and temperature. The composition of the other elements was set...
constant. The software package calculates the phase fraction and the composition of the phases for a given temperature and alloy composition.

For the calculation of a phase diagram, the software needs a start point. This means a composition and a temperature at which it can calculate the equilibrium concentration and phase fraction. A thermodynamic database provides the information which the software requires to perform the calculations. Here, the database TCFE7 has been chosen, which is a database optimized for steels. After calculating the equilibrium concentration and phase fraction, it can be selected for which temperature region and element composition the phase diagram should be calculated. A typical result can be seen in Figure 2-7. The results of this calculation are interactive. It is possible to select a point defined by temperature and composition and calculate from this the phase fractions and the composition of the phases. These values can be tabulated as well. This allows for instance, seeing the equilibrium concentration of a specific phase in dependence of the temperature.

3.8.2. Calculations with DICTRA

As mentioned on page 8, DICTRA can be used to calculate diffusion controlled phase transformations and diffusion in general. It combines the thermodynamic data provided by Thermo-Calc with the kinetic data stored in its own database. The simulations itself have to be 1-dimensional [27]. Before the calculations can be started, the following has to be defined:

- The size of the simulated cell
- The phases which should be taken into account
- The composition of the phases
- The temperature in dependence on time
- The geometry of the simulation

The cell is the basis of the simulation. Its size can be defined flexibly. One has to specify whether the cell should be closed or not. A closed cell describes a system where no exchange of elements with their surrounding can occur ([98] p. 14). This kind of boundary condition was used for the performed simulations.

For a successful simulation the phases should be taken into account must be decided. For the selected phases, the software loads the thermodynamic and the kinetic data. Following this, one has to determine whether a phase is active or inactive. For active phases, the size, the composition and the grid point density have to be defined. The composition does not have to

3 If a phase is defined as an inactive phase, it does not take part in the simulation as long as the driving force for its precipitation is not exceeded. When the driving force is exceeded, it takes part in the simulation. In contrast, an active phase joins the simulation right from the start [98].
be constant in a phase. It is possible to read-in the composition data from a file; as well as it is possible to define a function, which relates the position in the cell with a specific composition. Between the grid points the program tries to equilibrate the chemical potentials. An inactive phase can be located next to an active phase. It starts to grow automatically when it gets thermodynamically stable. In contrast to an active phase, the grid points are set up automatically by DICTRA. The composition of the inactive phase is the equilibrium composition at the temperature where it starts growing.

The temperature has to be defined in dependence of the time. For different time periods the temperature can be set up differently. A constant temperature is possible as well as a function, which describes the temperature in dependence of the time.

Even though DICTRA can only calculate 1-dimensional problems, certain geometries of the diffusion front can be taken into account. These are the planar, the cylindrical and the spherical diffusion interface [27]. All these geometries can be described with one space variable. For the study at hand, the planar geometry was used.
4. Analysis of the laboratory-processed steel

In this section, the results of the in-lab processed material will be presented. The microstructure as well as the mechanical properties were analysed with different techniques to allow a comparison between both. At the end the results will be discussed and thermodynamical simulations will be presented in order to get a deeper understanding of the phase transformations occurring during the heat treatment.

4.1. Experimental Results

Two different hot rolled steel sheets provided in the form of 3.7 mm thick plates were analysed. The material was produced commercially in a steel plant. It was cut from the middle of the coiled steel strip with respect to the length and the width of the strip. Both materials were coiled at different temperatures. The P+F variant was coiled at a higher temperature compared to the B+M variant. It is apparent from Table 3 that both materials have the same composition, except for minor differences in the Mn and Cr content.

<table>
<thead>
<tr>
<th></th>
<th>C (Wt. %)</th>
<th>Mn (Wt. %)</th>
<th>Cr (Wt. %)</th>
<th>Si (Wt. %)</th>
<th>Fe (Wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P+F</td>
<td>0.138</td>
<td>1.82</td>
<td>0.41</td>
<td>0.25</td>
<td>Balanced</td>
</tr>
<tr>
<td>B+M</td>
<td>0.138</td>
<td>1.93</td>
<td>0.43</td>
<td>0.26</td>
<td>Balanced</td>
</tr>
</tbody>
</table>

Table 3: Average composition of both steel variants.

The applied heat treatments were performed using a dilatometer. In order to assess the evolution of the properties of the different steels during the heat treatment, the microstructure was checked by quenching the samples after different times of the heat treatments. This was done before the heat treatment (Point 1), after the isothermal part of the heat treatment (Point 2) and after complete heat treatment (Point 3). OM-images were taken to get an overview of the changes occurring during the applied heat treatment. WDX measurements helped to describe the evolution of the local distribution of the alloying elements. Hardness measurements were performed to correlate the changes in the microstructure with the changes in the mechanical properties. Extraction replicas were prepared and analyzed at point 1 and point 2. They showed the changes in the distribution and composition of the carbides present in both microstructures. EBSD measurements were used after complete heat treatment in order to analyze the martensite fraction, the grain size of ferrite and the KAM. TEM was used in addition to reveal the nature of microstructural features, which were too small to be analyzed with EBSD.
Figure 4-1: Phase diagram of the steels. The used composition is the average composition of both materials. TC was used to perform the calculation.

4.1.1. Results of the dilatometer experiments

The dilatometer experiments were performed on both microstructures, whereby for both microstructures 10 specimens were annealed. The applied heat treatment can be seen in Figure 4-2. 5 specimens were completely heat treated (Point 3) and for 5 specimens the heat treatment was interrupted after the isothermal part of the heat treatment (Point 2). The plateau temperature was 840 °C, which is in the pure austenite region of both steel types (cf. Figure 4-1). The length change in dependence of temperature can be seen in Figure 4-3. Two curves typical of both materials are plotted in the Figure. During heating up, the growth of austenite is indicated by the deviation of the curve from the linear relation between temperature and time. It was measured for both specimens for all performed heat treatments. The average start temperature for B+M was (737 ± 4) °C and (755 ± 3) °C for P+F. This indicates that for both microstructures the growth of austenite started at nearly the same temperature. The cooling curves, plotted in Figure 4-3, show distinct differences between both materials. In the case of the P+F microstructure the transformation of fcc to bcc begins much earlier than in the case of B+M. For both materials 5 samples were analyzed. The exact transformation temperature for B+M was (510 ± 1) °C and (668 ± 8) °C for P+F. Here, the error is the standard deviation of the measurements. The martensite start temperature
was determined for both variants as well. For B+M it was $(225 \pm 23) \degree C$ and for P+F $(161 \pm 12) \degree C$.

![Graph](image)

**Figure 4-2**: Heat treatment applied to the dilatometer samples. The temperature is measured with a thermo element directly connected to the sample.

![Graph](image)

**Figure 4-3**: Length change in dependence on temperature. a) shows the results for B+M. b) shows the results for P+F. The red circle indicates the transformation to austenite. The blue circle shows the starting point of the transformation from austenite to bcc.

### 4.1.2. Microstructure analysis by OM

OM-images were taken before and after the complete heat treatment. It can be seen in Figure 4-4 a) that at the beginning, the P+F variant consists of a ferrite matrix with pearlite islands embedded. Additionally, there are several small carbides found in the ferrite. The B+M variant consists of ferrite, martensite and bainite regions (cf. Figure 4-4 b). In Figure 4-5, both steels are shown after complete heat treatment. Even though the contrast is quite different in both steels, both consist of a ferrite matrix with embedded martensite islands. Additionally the P+F variant contains some regions which look like undissolved pearlite.
Figure 4-4: OM images of the microstructure before heat treatment. a) shows the P+F variant. In b) the B+M variant is shown.

Figure 4-5: OM images of the microstructure after complete heat treatment. a) shows the P+F variant. In b) the B+M variant is shown.

4.1.3. Mechanical properties of the material
The Vickers hardness was measured at different points of the heat treatment. After hot rolling the P+F variant is softer, compared to the B+M material. This was expected since it is known that martensite and bainite harden the material more than pearlite. After interrupting the heat treatment at point 2, both specimens have nearly the same hardness. At the end of the heat treatment the B+M variant is harder again.
4. Analysis of the laboratory-processed steel

4.1.4. Distribution of the alloying elements

The distribution of the alloying elements was measured using WDX. Figure 4-7 shows the distribution of Mn and Cr of the hot rolled P+F microstructure. One can see that Mn and Cr enrichments are found at the same positions. Because of the lower average content of Cr, its signal is much lower. Hereafter, only the Mn signal will be presented due to its higher signal.

Figure 4-6: Development of the hardness during the heat treatment. For every measurement point 8 measurements were performed and the average value was calculated. The error is the standard deviation of the measurements.
Figure 4-7: WDX measurement of P+F after hot rolling. The Mn and the Cr signal were obtained. The measurement was performed under the following conditions. 500 nm step size, 20 nA beam current, 15 kV accelerating voltage, 1 detector for Mn and 1 detector for Cr.
The WDX measurement of the B+M variant after hot rolling is presented in Figure 4-8. The low C regions show the presence of ferrite. Areas with higher C content indicate the presence of martensite, bainite and some single carbides. The Mn concentration is not distributed homogeneously. Mn enrichments are distributed in the form of a banded structure, which is caused by crystal segregation. In all performed mappings, the Mn concentrations varied between 1.5 Wt. % and 2.3 Wt. %. The distribution of the alloying elements in P+F can be seen in Figure 4-9. Here, C is enriched in the pearlite islands and in the single carbides lying in the ferrite regions. In this figure again, ferrite is indicated by a low C concentration. In P+F, the distribution of Mn is different compared to B+M. Besides the enrichments found in the form of bands, high Mn spots are visible. They seem to correlate with the high C regions. In order to check this correlation for P+F in more detail, the C map and the Mn map were overlaid by using Photoshop (Version CS4). 100 points with a high Mn content were marked and it was checked whether they were located at the same position as the high C regions or not. For the hot rolled state, 100 % of the high Mn points were located at the same positions as the high C regions. In addition to the Mn enriched regions, the WDX-maps shows areas depleted of Mn, which means that they have a lower Mn concentration than the average Mn content. Further WDX analysis showed that the lowest concentration was $(1.30 \pm 0.05)$ Wt. %.
Figure 4-8: WDX measurement of B+M hot rolled (Point 1). The Mn and the C signal were obtained. The measurement was performed under the following conditions. 300 nm step size, 40 nA beam current, 12 kV, 1 detector for C and 2 detectors for Mn.
Figure 4-9: WDX measurement of P+F hot rolled (Point 1). The Mn and the C signal were obtained. The measurement was performed under the following conditions. 300 nm step size, 40 nA beam current, 12 kV, 1 detector for C and 2 detectors for Mn.
After interrupting the heat treatment (Point 2), the distribution of C changed for both steel types. Figure 4-10, which presents the WDX results for B+M, shows a much more homogeneous distribution of C compared to the hot rolled material (Point 1). This means that the WDX map confirms the assumption that the material is fully martensitic. In addition a few high C spots can be found, which will be discussed later on. For B+M, the Mn is distributed similarly to the material before the heat treatment.

In contrast to B+M, the WDX map of P+F does not show a completely homogeneous distribution of C (cf. Figure 4-11). Besides the large areas, which show a homogeneous C content, small regions with a lower C content than the average one can be found. Similar to B+M, the Mn is distributed as in the material before the isothermal heat treatment, which means that high Mn spots and Mn depleted zones are both present. Comparing the C and the Mn maps reveals that the low C regions are always located at low Mn regions. In contrast to the hot rolled material, the correlation between the high Mn spots and the high C regions has mostly disappeared. Only 7% of the high Mn zones are located at position of high C content.

In order to find an explanation for the high C spots present in B+M and P+F after the isothermal part of the heat treatment a WDX mapping of the Ti content was performed additionally. The results are presented in Figure 4-12. The correlation between Ti and C was checked the in same way as it was done for Mn and C. 92% of the high C zones correlate with Ti and only 8% correlate with Mn. This implies that most of the high C zones are caused by Ti carbonitrides.
Figure 4-10: WDX measurement of B+M after isothermal heat treatment (Point 2). The Mn and the C signal were obtained. The measurement was performed under the following conditions. 300 nm step size, 40 nA beam current, 12 kV, 1 detector for C and 2 detectors for Mn.
Figure 4-11: WDX measurement of P+F after isothermal heat treatment (Point 2). The Mn and the C signal were obtained. The measurement was performed under the following conditions. 300 nm step size, 40 nA beam current, 12 kV, 1 detector for C and 2 detectors for Mn.
Figure 4-12: WDX: measurement of P+F after isothermal heat treatment (Point 2). The C and the Ti signal were obtained. The measurement was performed under the following conditions. 300 nm step size, 40 nA beam current, 12 kV, 1 detector for C and 1 detectors for Ti.
After complete heat treatment, the distribution of C changed for both steel types. C is enriched in the form of islands and depleted in the rest of the matrix (cf. Figure 4-13 and Figure 4-14). This correlates with the microstructure found by OM (cf. Figure 4-5). For B+M, the C rich islands often have a higher C content at the boundary. This effect is only rarely visible for P+F. The Mn distribution of B+M is the same as it was before the heat treatment. The crystal segregations are still visible (cf. Figure 4-13). In the case of P+F, Mn is also distributed as in the material before the heat treatment. This means that enrichments in the form of spots, Mn depleted zones and the banded structure are still present. The correlation between Mn and C was checked and it was found that 97% of the high Mn zones correlate with high C zones.
**Figure 4-13:** WDX measurement of B+M after complete heat treatment (Point 3). The Mn and the C signal were obtained. The measurement was performed under the following conditions. 300 nm step size, 40 nA beam current, 12 kV, 1 detector for C and 2 detectors for Mn.
Figure 4-14: WDX measurement of P+F after complete heat treatment (Point 3). The Mn and the C signal were obtained. The measurement was performed under the following conditions. 300 nm step size, 40 nA beam current, 12 kV, 1 detector for C and 2 detectors for Mn.
4.1.5. Evolution of the carbides

With the intention of analysing the carbides present in the material, extraction replicas were prepared. This was done for B+M as well as for P+F before and after the heat treatment. In order to distinguish the different carbides and to quantify their composition, EBSD and EDX were used.

4.1.5.1. Analysis before heat treatment

Figure 4-15 presents an overview of the different carbides extracted from both microstructures before heat treatment. In the case of P+F, the former pearlite regions and the single carbides located in ferrite are visible. In the image of the extraction replica created from B+M, the former bainite regions are present. The EBSD measurements revealed that in the case of B+M the lamella shaped carbides are all cementite. This was not the case for P+F. In addition to cementite M23C6 was identified, whereby cementite was located in former pearlite regions as well as in the ferrite regions but M23C6 was only found in ferrite regions. Additionally, Ti carbonitrides were found in both microstructures.

For both microstructures the composition of the carbides was determined. Therefore, the carbides were identified with EBSD and afterward analysed by using EDX. The applied correction model was P/B-ZAF. The results are presented in Table 4. Compared to the average composition (cf. Table 3), the carbides present in B+M did not enrich with substitutonal elements. In the case of P+F, cementite as well as M23C6 was enriched with substitutonal elements. In M23C6 the enrichments found were slightly larger compared to cementite.

Due to the fact that the extracted cementite lamellae did not only come from the surface of the examined specimens (B+M and P+F before heat treatment) but also from the inside of the volume of the specimens, the lamellae tilted over with each other and it was not possible to determine reliably the volume fraction of carbides by applying large area EDX mappings and to determine from that the volume fraction of cementite. The obtained area fractions of cementite were much too high. Values up to 30 % were found. In order to discuss the evolution of the volume fraction of the Fe carbides, the following assumptions were made for the hot rolled material:

- All C is bound in cementite.
- Ferrite and cementite have the same density.

The volume fraction of cementite can then be described by

\[
V_{\text{Fe}_3\text{C}} = \frac{c_{\text{steel}} c_{\text{Fe}_3\text{C}}}{c_{\text{steel}} c_{c\text{Fe}_3\text{C}}}
\]
Here, $V_{Fe3C}$ is the volume fraction of cementite, $c_{C-steel}$ is the concentration of C in steel in Wt. % and $c_{C-Fe3C}$ is the concentration of C in cementite in Wt. % (6.67 wt. %). Using the average C concentration of both steel types (0.138 Wt. %) leads to $V_{Fe3C} = 2.1 \%$.

![Figure 4-15: SEM-STEM image of the extracted carbides before heat treatment. The measurement was performed at 25 kV. a) shows carbides from P+F. b) shows carbides from B+M.](image)

<table>
<thead>
<tr>
<th></th>
<th>C (Wt. %)</th>
<th>Mn (Wt. %)</th>
<th>Cr (Wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B+M cementite</td>
<td>6.67</td>
<td>1.9 ± 0.2</td>
<td>0.4 ± 1</td>
</tr>
<tr>
<td>P+F cementite</td>
<td>6.67</td>
<td>14.6 ± 1.0</td>
<td>3.0 ± 0.2</td>
</tr>
<tr>
<td>P+F M23C6</td>
<td>5.34</td>
<td>19.6 ± 1.1</td>
<td>4.1 ± 0.3</td>
</tr>
</tbody>
</table>

Table 4: Composition of the Fe carbides present in the microstructures. 6 measurements were performed to quantify the composition of the cementite in B+M. 8 compositions were obtained for the cementite and M23C6 present in P+F. The error is the standard deviation of the measurements.

4.1.5.2. **Analysis after complete heat treatment**

After complete heat treatment, the amount of Fe carbides was reduced in both steel variants. For B+M, there were even no Fe carbides left. In the case of P+F some Fe carbides were still present. A detailed analysis of several SEM-STEM-images revealed that all Fe carbides, which survived the heat treatment, were surrounded by martensite. In contrast, no Fe carbides were found in ferrite regions. The area fraction of Fe carbides was determined for P+F. To this end, a large area EDX measurement was performed. It led to an area fraction of $A_{Fe3C} = 0.051 \%$. The fact that all Fe carbides after complete heat treatment were mostly round particles and no lamellae made the assumption reasonable that the area and the volume fraction are the same after complete heat treatment. By comparing the results with the amount of carbides measured before heat treatment, it can be derived that only 2.6 % of the original amount of Fe carbides was inherited. Quantitative EDX measurements were performed the same way as for the samples without heat treatment (cf. p. 71). For cementite, the Mn content did not change within the measurement tolerances; whereas the Cr content...
increased slightly (cf. Table 5). In the case of M23C6, the Mn content did not change as well but the Cr content raised a lot.

<table>
<thead>
<tr>
<th></th>
<th>C (Wt. %)</th>
<th>Mn (Wt. %)</th>
<th>Cr (Wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P+F cementite</td>
<td>6.67</td>
<td>13.9 ± 1.6</td>
<td>5.6 ± 1.8</td>
</tr>
<tr>
<td>P+F M23C6</td>
<td>5.34</td>
<td>18.8 ± 1.5</td>
<td>15.5 ± 2.4</td>
</tr>
</tbody>
</table>

Table 5: Composition of the Fe carbides present in P+F after complete heat treatment. 5 compositions were obtained for the cementite and 6 were performed for the M23C6. The error is the standard deviation

4.1.6. EBSD measurements after complete heat treatment

In order to find an explanation for the different hardness values of both steel variants, the microstructure was analysed using EBSD. The large area EBSD technique described on page 41 was used for the measurements. For both microstructures, the measurement was performed at 15 kV with a step size of 100 nm. The grain size of ferrite, the kernel average misorientation (KAM) and the martensite content were determined. In the case of the P+F microstructure, 95 maps with an edge length of ca. 20 µm were obtained. The total size of the measured maps covered a rectangle of 380 µm x 100 µm and was distributed on a rectangle of 1100 µm x 670 µm. In total, 6385 ferrite grains were analysed to determine the KAM and the average grain size. For B+M, the size of the small maps was the same. Here, 34 maps were measured. They covered a rectangle of 646.3 µm x 40 µm and were distributed over a rectangle of 7750 µm x 330 µm. The bcc-iron was separated into ferrite and martensite. 2284 ferrite grains were analysed to determine the KAM and the average grain size. As long as not described differently, the KAM was calculated using the 1st neighbour. In order to derive the GND density, Equation (3.3) was used. The required lattice constant was determined with XRD. A value of \( d = 2.867 \cdot 10^{-10} m \) was found for bcc-iron. The results of the measurements can be found in Table 2. It illustrates that the B+M microstructure has a higher content of martensite compared to P+F. The average GND density shows higher values as well, not only in the case of the bcc-iron, which includes martensite and ferrite, but also for the pure ferrite. The grain size of ferrite found for B+M is a little bit smaller compared to the values found for P+F.

<table>
<thead>
<tr>
<th></th>
<th>Ferrite grain avg. diameter (µm)</th>
<th>Martensite area fraction (%)</th>
<th>bcc-iron average GND density ( \frac{1}{m^2} )</th>
<th>Ferrite average GND density ( \frac{1}{m^2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>P+F</td>
<td>4.92</td>
<td>7.3 ± 1</td>
<td>2.53⋅10^{14} ± 0.5⋅10^{14}</td>
<td>2.34⋅10^{14} ± 0.4⋅10^{14}</td>
</tr>
<tr>
<td>B+M</td>
<td>4.30</td>
<td>14.6 ± 1.2</td>
<td>3.44⋅10^{14} ± 0.14⋅10^{14}</td>
<td>3.09⋅10^{14} ± 0.14⋅10^{14}</td>
</tr>
</tbody>
</table>

Table 6: Results of the large area EBSD measurement, P+F and B+M were analysed. The ferrite grain avg. diameter is weighted by area and not by number.
Figure 4-16: Example of the GND density distribution in B+M and P+F. a) shows the distribution in B+M and b) in P+F. The light blue lines indicate the boundaries between the single maps of the large area scan and the light blue regions in the maps highlight the martensite.

Figure 4-16 presents two small GND density maps, characteristic of P+F and B+M. They were obtained during the large area EBSD scans. Here, only the GND density of the ferrite grains is plotted. It is obvious that the GND density is not distributed in the same way in both microstructures. P+F contains grains, where the GND density reaches quite high values and grains where the GND density is quite low. B+M has only ferrite grains where the GND density is quite high.

4.1.7. **EBSD combined with WDX**

In order to understand the distribution of the GND density in the P+F microstructure after complete heat treatment, a WDX measurement was combined with an EBSD map by using Photoshop (Version CS4). As a result, it was possible to plot the distribution of Mn and the GND density at the same position. This is shown in Figure 4-17. It is apparent from this map that at the position of high Mn bands the chance is higher to find regions with a high GND density and vice versa. In addition to the crystal segregations, the low Mn zones seem to correlate with regions of a low GND density. To check this correlation, 53 low Mn regions were marked using Photoshop and it was checked, whether they were located in regions of low GND densities or not. All marked regions were located in areas of low GND density or directly at the boundary. Whether a GND density region is a low GND density region or not,
was checked by comparing the regions with their neighbourhood. When a region had a significantly lower GND density than the neighbouring one, it was marked as a region with a low GND density.

**Figure 4-17:** Combined GND density and Mn map of P+F after complete heat treatment. a) shows the GND density map; b) shows transparent overlay of the Mn signal; c) shows a non-transparent overlay of the Mn signal. The original Mn map had to be transformed due to drift during the measurement. The light blue regions are martensite. The EBSD map was performed with a step size of 150 nm. The step size of the WDX measurement is 300 nm.

Figure 4-18 shows the correlation between the GND density and the C distribution. The contrast of the C signal was increased, to show small variations more clearly. As expected, the martensite islands are strongly enriched with C. Comparing the regions with a low and a high GND density in terms of the C content, reveals that at regions with a low GND density the C content is slightly lower compared to regions with a high GND density. In Figure 4-19 the GND density and the IQ are compared. In the IQ map, a lamella microstructure is visible. Comparing the GND density map and the IQ map reveals that regions with a high GND density are at the same position as the lamella like microstructure. A more detailed analysis of the lamella like microstructure will be given in the following chapter.
Figure 4-18: Combined GND density and C map of P+F after complete heat treatment. a) shows the GND density map; b) shows transparent overlay of the C signal; c) shows a non-transparent overlay of the C signal. The original C map had to be transformed due to drift during the measurement. The EBSD map was performed with a step size of 150 nm. The step size of the WDX measurement is 300 nm.

Figure 4-19: Comparison of the GND density and the IQ of P+F after complete heat treatment. a) shows the pure GND density map; b) shows a mixed map of the GND density and the IQ; c) shows only the IQ map.

4.1.8. Lamella like microstructures after complete heat treatment

As mentioned above (p. 57), the P+F microstructure after complete heat treatment showed regions which looked like undissolved pearlite under the optical microscope. In order to study these regions in more detail, SEM-pictures were taken. An area typical of the examined microstructure is presented in Figure 4-20. Here, the surface was etched with Nital which is known to etch preferentially low C zones. The lamellae were etched less than the surrounding
4. Analysis of the laboratory-processed steel

matrix. This indicates a higher C content of the lamellae compared to the average content. In order to check whether these lamellae were cementite, extraction replicas of P+F after complete heat treatment were produced. An SE image of it can be seen in Figure: 4-21. The lamella microstructure is clearly visible, but there is no extracted cementite present. A high resolution EBSD measurement was performed as well. A combined IQ and phase map can be seen in Figure: 4-22. The lamella structure is indexed here as austenite or as low IQ bcc-iron. It is additionally apparent from this map that bigger lamellae have a higher chance to be indexed as austenite than smaller ones. Since the size of the lamellae was found to be very small and thus is at the limit of the resolution of EBSD, a TEM sample was prepared. This was done according to the method described on page 50. An overview of the prepared specimen is shown in Figure 4-23. The lamellae are visible due to their different contrast compared to the matrix. On the former specimen surface, some platinum is visible which was deposited there during the preparation of the specimen. Orientation imaging microscopy was performed on the lamellae using ASTAR [94-96]. This was done for several lamellae. The measurements showed only bcc-iron. Austenite, cementite or other Fe carbides were not found. Figure 4-24 shows a single lamella analysed with ASTAR. The crystal structure is always bcc. In the deposited platinum the IQ is very low, since there is no crystal structure present which could be indexed. Also the grain boundaries found in platinum are without any meaning. In the bcc in contrast, high angle grain boundaries are found in the lamella as well as between the lamella and the matrix. In order to check the local composition at the lamellae, EDX line scans were performed by using the SEM in STEM mode. As it can be seen from Figure 4-25, the Mn content varies in dependence on the position. It is higher at the position of the lamellae and lower in between.

Figure 4-20: SEM pictures of the lamella like structures. The specimen has been etched with Nital in order to make the lamellae visible.
Figure: 4-21 SE image of the extraction replica of P+F after complete heat treatment.

Figure: 4-22 Combined IQ and phase map of P+F after complete heat treatment. The used step size is 50 nm. Red indicates austenite and green indicates bcc-iron.
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Figure 4-23: STEM image of the TEM sample of the lamella like structure. The used accelerating voltage was 200 kV and the spot size was set to 1.5 nm.

Figure 4-24: Single lamella analysed with ASTAR. The used step size was 5 nm.
Figure 4-25: Results of the EDX scan performed on the lamellae in SEM in STEM mode. On the left hand side the Mn content in dependence on the position is plotted. On the right hand side the position of the scanned line is shown.

4.2. Discussion and open questions

In order to better pre-structure the discussion, the results are summarized in the following:

- The main difference between both microstructures, namely, the P+F and the B+M microstructure, is the distribution of Mn. For B+M, coiled at lower temperatures, the Mn content only shows inhomogeneities in form of crystal segregations, created during solidification. For P+F, coiled at significantly higher temperatures, Mn is enriched in carbides and depleted in other zones. These inhomogeneities are formed, as it will be discussed later, during the cooling period after coiling by diffusion of substitutional elements into the carbides. Local inhomogeneities survive the heat treatment, even though the carbides responsible for them were nearly completely dissolved.

- Before the heat treatment, the B+M microstructure is harder than P+F. Interrupting the heat treatment after the intercritical annealing step leads to microstructures which both have the same hardness. After complete heat treatment, B+M is again harder than P+F.

- For P+F, the reaustenization is not completed after the isothermal part of the heat treatment. This is indicated by C and Mn-depleted zones, which correspond to untransformed ferrite.
• During cooling down, the fcc-bcc transformation begins at higher temperatures for P+F than for B+M. After complete heat treatment, the martensite content as well as the average GND density in ferrite and bcc-iron (ferrite and martensite) is higher for B+M than for P+F.

• After complete heat treatment, the P+F microstructure shows a lamella-like microstructure which looks like incompletely dissolved pearlite. Extraction replicas, EBSD, EDX and OIM in TEM show, that the lamellae are neither cementite nor M23C6 but austenite or martensite. The lamellae are found at positions of higher Mn content. Only 2% - 2.5% of the original amount of carbides are inherited.

4.2.1. Enrichment of carbides with substitutional Elements
It is a fact of common knowledge that carbides can enrich with substitutional elements like Mn and Cr [20, 21, 99]. Figure 4-26 shows the equilibrium enrichment of cementite with substitutional elements in dependence on the temperature of the present material, as calculated with Thermo-Calc. One can see that the lower the temperature the higher is the enrichment of M3C with substitutional elements in equilibrium. Of course, due to limited diffusion, these values are not found in real samples. The dashed line shows the degree of Mn enrichment of the analyzed cementite in P+F and the dotted and dashed line shows the enrichment measured in B+M. For B+M the concentrations of the substitutional elements is near the average concentration of the steel. It can be concluded that here the temperature, during which the carbides were formed, was too low to allow the formation of carbides following LEP. The formation must have occurred under LENP or PE, because it is known that under this growth regime the substitutional elements do not partition. The evolution of the enrichments of the substitutional elements, caused by the cementite lamellae, during the heat treatment will be shown and discussed on the base of some DICTRA calculations in Chapter 4.3.2.
Figure 4-26: Equilibrium concentration of M3C depending on temperature. The average composition of P+F was used to calculate the concentrations with TC.

4.2.2. Growth of bcc during cooling down

In contrast to B+M, the WDX measurements of P+F after the isothermal part of the heat treatment (Point 2) showed an incomplete reaustenization of the matrix. It was found that 3% of the matrix was not reaustenized. These regions were correlated with low Mn zones. The phase diagram of Mn and Fe (cf. Figure 2-8) shows clearly that a lower Mn content increases the formation temperature of austenite. This means that during heating up and the isothermal part of the heat treatment, the growth of austenite into ferrite should have been slower in regions of low Mn content compared to regions with a higher Mn content. This could be the reason, why the ferritic regions found at point 2 of the heat treatment were always located in low Mn regions. For a deeper understanding of the role of the Mn depleted zones, some DICTRA calculations were performed. The results will be shown in Chapter 4.3.1.

During cooling down of P+F, ferrite started to grow at higher temperatures compared to B+M, which was indicated by the dilatometer experiments. The reasons for this are the areas of inherited ferrite, which can start to grow during cooling down without any nucleation. In the case of B+M, no ferrite survived the heat treatment. Hence, new ferrite had to nucleate during cooling down. In general, nucleation processes need time and a certain degree of undercooling, which means that in the case of B+M the transformation of fcc to bcc begins at a lower temperature (510 °C ± 1 °C) compared to P+F (668°C ± 8 °C).

The difference in the formation temperature of bcc for P+F and B+M is responsible for many of the found results.
The often found enrichment of C at the boundaries of martensite and ferrite in B+M can be explained by the later transformation. At the lower transformation temperature C is much less mobile and has less time to distribute homogeneously in the austenite.

The dissimilar martensite content is also a result of the different growth temperatures of bcc for P+F and B+M. Compared to P+F, the ferrite in B+M has less time to grow. This leads to a higher content of austenite, which transforms to martensite during cooling down to room temperature.

The difference in the hardness also depends on the different formation temperature of the B+M compared to P+F. This will be discussed in detail in the next section.

**4.2.3. Evolution of the hardness**

After complete heat treatment a correlation between the martensite content and the hardness of the specimen can be found. B+M is harder compared to P+F and contains at the same time more martensite. Since it is known that martensite hardens the material [13], the higher martensite content for B+M could be one reason for the increased hardness compared to P+F. Additionally, the GND density is not the same for both specimens. This is important since Ashby et al showed that GNDs harden the material as well [78]. In ferrite and in bcc-iron (ferrite and martensite combined) B+M shows a higher GND density compared to P+F. It seems to be obvious that besides the higher martensite area fraction of B+M the higher GND density of B+M hardens the material additionally. A closer look at the distribution of the GNDs in ferrite showed that P+F contained grains, where the GND density is quite high and grains where it is lower. The B+M variant contained only ferrite grains with quite a high GND density. It is not very likely that the higher average GND density of ferrite in B+M is mainly caused by the higher martensite content of B+M as reported in the study of Calcagnotto et al. [81]. If this were the case, higher GND density values should only be found at the boundaries between martensite and ferrite and not in the middle of the ferrite grains as in the present study (cf. Figure 4-27). A more likely reason for the lower values of the average GND density in ferrite in P+F could be that the growth of bcc in P+F starts at higher temperatures compared to B+M. The growth of bcc at higher temperatures could occur with a more diffusional character as the growth of bcc at lower temperatures. From the example of the growth of martensite it is known that a displacive transformation produces more dislocations compared to a diffusional one. For bainite it was shown as well that bcc formed at higher temperatures has a lower dislocation density compared to bcc formed at lower temperatures [39]. As pointed out above, P+F contains ferrite grains with quite a high average GND density and ferrite grains with a much lower average GND density (cf. Figure 4-28). The experiments revealed two reasons for this behaviour, which will be explained in the following. EBSD
measurements showed that ferrite grains with a high average GND density often contain the lamella shaped microstructure caused by the former pearlite. As shown in Chapter 4.1.8, it was found that the lamellae were typically martensite or austenite. For martensite it is known that it deforms during its formation plastically the neighbouring ferrite, which promotes the formation of high GND density values in the ferrite [81]. The dilatometer experiments showed additionally that the growth of bcc started for P+F at quite high temperatures but ended at much lower temperatures. If one assumes that the GND density of ferrite depends on the transformation temperature ferrite regions with the lower average GND densities should be formed at higher temperatures compared to the regions with the higher average GND density. A sharp boundary, in terms of the GND density, between ferrite formed at higher temperatures and ferrite formed at lower temperatures cannot be expected, since applied cooling process was continuous.

In comparison to the other effects, the inherited carbides influence the hardness of P+F only on a minor level. For P+F it was shown that only 2.6 % of the original amount of carbides was inherited. This implies that 97.4 % of the C is incorporated in the martensite and contributes to its hardening. For B+M, 100 % of the C can be used by the martensite, since no carbides were inherited during the heat treatment. A difference of 2.6 % means that for P+F the free C content is 0.134 Wt. %.

![EBSD map](image_url)

**Figure 4-27:** High resolution EBSD map of B+M after complete heat treatment. The left image shows the IQ and the right image shows the GND density map. The step size of the measurement is 50 nm. In order to calculate the GND density, the 3rd neighbour KAM value was calculated. The black lines show the high-angle grain boundaries (15°-180°).
In order to prove, whether an alternative heat treatment would change the mechanical properties of the P+F microstructure a heat treatment was applied where the plateau temperature was increased up to 900 °C. The dilatometer curve of the experiment is plotted in Figure 4-29. It shows clearly that the growth of bcc starts here at much lower temperatures compared to P+F heated up to 840 °C (cf. Figure 4-3 b)). Actually, it looks more like the dilatometer curve obtained from B+M at 840 °C (cf. Figure 4-3 a)). In order to examine whether reaustenization was completed, the heat treatment was interrupted after the isothermal part of the heat treatment and a WDX measurement was performed. Figure 4-30 presents the results of the measurements. The completely homogeneous distribution of C, except from the Ti carbonitrides, even in the small Mn depleted zones, indicates that the reaustenization was completed. The heat treatment at the higher temperature led to a higher hardness as well. The results of the indentations are shown in Figure 4-31. It was measured after complete heat treatment (Point 3). The graph illustrates clearly that the hardness of P+F heated up to 900 °C is more comparable to the hardness of B+M heated up to 840 °C than the hardness of P+F heated up to 840 °C. A possible reason, why the hardness was still a little bit lower is that the austenite annealed at higher temperatures could have a larger grain size.
Figure 4.29: Dilatometer curve of P+F heated up to 900 °C.
Figure 4-30: WDX measurement of P+F quenched after heat treatment at 900 °C (Point 2). The Mn and the C signal were obtained. The measurement was performed under the following conditions. 300 nm step size, 40 nA beam current, 12 kV, 1 detector for C and 2 detectors for Mn.
Figure 4-31: Hardness of the material measured at different points of the heat treatment. For every measurement point 8 measurements were performed and the average value was calculated. The error is the standard deviation of the measurements.

4.3. DICTRA Simulations

As pointed out in the last section, it was not possible to understand all aspects of the transformations occurring during the heat treatment of both steel types. In order to gain a deeper scientific understanding of the role of the Mn depleted zones and the evolution of the enriched cementite lamellae a few DICTRA calculations were performed. The first of the two following subchapters discusses the role of the Mn depleted zones during the growth of austenite into ferrite during the intercritical annealing. The second one deals with the evolution of the enrichments of substitutional elements caused by cementite lamellae.

4.3.1. The influence of Mn depleted zones on the growth of austenite

To understand the role of the Mn depleted zones during the reaustenization of the P+F variant, a set of DICTRA simulations was performed. Figure 4-32 shows the start distribution of the elements for one of the performed simulations. The red line indicates the boundary between the austenite (left) and the ferrite (right) regions. The Mn depleted zone is located in the ferrite region. Its thickness is 2.5 µm. The start temperature of the simulation is 820 °C. It is increased to 838 °C in 6 seconds and kept constant from this time on. In austenite as well as in ferrite, the Mn content was set to 1.5 Wt. %. Only in the Mn depleted zone the content was set to 0.5 Wt. %. As shown in the Figure, the C content was set to 0.14 Wt. % in the austenite and to 0 Wt. % in the ferrite region. Figure 4-33 a) shows that the growth speed of the phase
boundary varies in dependence of time. At the beginning as well as at the end it grows very fast. Between $t = 8\, \text{s}$ and $t = 118$ the growth speed is reduced. As it can be revealed from Figure 4-33 b) and c), at this time the phase boundary was in the Mn depleted zone. After the minimum in the Mn depleted zone, the growth speed increased very fast. In order to reveal the influence of the height of the Mn depletion, the simulation was performed for several Mn contents in the depleted zone. The results are shown in Figure 4-34 a). It illustrates clearly that with increasing Mn content the interface is slowed down less; an increase of the Mn content by 0.1 Wt. % halves the time that the interface is located in the depleted zone. Mn contents higher than 0.8 Wt. % did not slow down the interface efficiently any more. In order to reveal the influence of the thickness of the depleted zone, the simulation was performed for different thicknesses of the depleted zone, but with a constant Mn content of 0.5 Wt. %. The C content in the austenite was 0.13 Wt. %. As shown in Figure 4-34, a larger thickness of the depleted zone, slows down the interface for longer times compared to thinner regions. In a realistic situation in which the ferrite survives the complete 84 seconds of the isothermal part of the heat treatment, the ferrite/austenite boundary is not allowed to cross the Mn depleted zone in a time shorter than 168 seconds in the appropriate simulation. This applies because in reality austenite may not just grow from one side into the Mn depleted region but from two sides. Figure 4-34 shows that a depletion down to 0.5 Wt. % Mn and a thickness of the depleted zone between 2.8 µm and 3.0 µm is needed to stabilize the ferrite for such a long time. Another possible combination is a Mn concentration of 0.4 Wt. % and a thickness of 2.5 µm. The lowest values for the Mn content in the depleted zones measured with WDX were 1.25 Wt. %. This implies that the simulations do not perfectly agree with the real situation.
Figure 4-32: Start conditions of the first variant of the DICTRA simulation dealing with the influence of the Mn depleted zone. A planar geometry was used for the simulation.

Figure 4-33 a) shows the position of the austenite ferrite interface in dependence of time. b) shows the profile of Mn and C at $t = 8\,\text{s}$. c) shows the profile at $t = 118\,\text{s}$.

Figure 4-34: Influence of time and thickness on the Mn depleted zone on the growth of austenite. a) shows the time that the interface is in the depleted zone in dependence of the thickness of the Mn depleted zone. b) shows the time that the interface is in the depleted zone in dependence on the Mn content in the depleted zone.

In order to prove whether a Mn depleted zone with a Mn content of 1 Wt. % could slow down the interface between austenite and ferrite long enough to allow the ferrite to survive the
isothermal annealing, the following simulation was set up. Here, the start temperature was 755 °C. This is the temperature at which the dilatometer curves showed the start of the reaustenization of the microstructure. The complete applied heat treatment can be seen in Figure 4-35 b). It shows that after the isothermal part of the heat treatment the material is quenched. In accordance with the dilatometer curves, the quenching speed was set to 100 K/s. It was assumed that all C is located in the former pearlite region but all pearlite has already been transformed into austenite. The distribution of C and Mn at t = 0 is plotted in Figure 4-35 a). The Mn content is the same (1.5 Wt. %) everywhere except for the right part of the ferrite region. The size of the cell is 18 µm, which is half of the longest distance measured by SEM between two pearlite regions. The average C content of the cell was set to 0.138 Wt. %. A second simulation was also set up. It was performed using nearly the same conditions as for the simulation described before. The only difference was the distribution of Mn. It was constant everywhere which means that no depletion of Mn was taken into account. The results of both simulations are shown in Figure 4-36. For the simulation where Mn depletion was taken into account, the ferrite region shrinks after 60 seconds so slowly that a small ferrite region survives the complete isothermal part of the heat treatment. During quenching, this ferrite region started to grow again and reached a total thickness of 1.7 µm. Because only half of a Mn depleted zone was simulated, the total thickness of the ferrite region is 3.4 µm. For the simulation where there is no Mn depletion present, the results were different. As it can be seen in the Figure, the interface was also fast at the beginning and slower after a few seconds, but the ferrite was not stabilized. After 60 seconds, which means roughly 35 seconds of the isothermal part, the ferrite was completely dissolved. This implies that during cooling down no ferrite can grow.

Figure 4-35: Start conditions of the DICTRA simulation dealing with the Mn depleted zone located at the end of cell. a) shows the start distribution of the alloying elements for the DICTRA simulation set up to study the role of the Mn depleted zone. A planar geometry was used for the simulation. b) shows the evolution of the temperature with time.
In order to explain the influence of the Mn depleted zone on the reaustenization of the material, a simulation similar to the one shown in Figure 4-36 was performed. Here, the only difference was that the simulated cell was expanded to the right side. This means that the size of the Mn depleted zone was doubled and afterwards the Mn concentration reached again a value of 1.5 Wt. %. The complete simulated cell had then a size of 23 µm. In general the driving force for the transformation from ferrite to austenite is correlated to the slope of the activity of C. The higher the slope of the activity the higher is the driving force for the transformation. It was found that slope of the activity of C was different for the both simulations, even though in both simulations the phase boundary was in both simulations located at the end of the depleted zone. In the simulation where the depleted zone was located at the end of the cell, the slope of the activity of C was smaller than for the simulation where the depleted zone was not at the end of the cell, which correlates with the fact that the stabilization ferrite needs less Mn depletion if it is located at the cell.

From the performed simulations it can be concluded that the Mn depleted zones kinetically stabilize the ferrite. The severity of the effect depends on several factors, which will be summarized and explained in the following:

- The lower the Mn content in the depleted zone, the stronger the interface is slowed down. This is due to the fact that low Mn contents stabilize ferrite at higher temperatures (cf. Figure 2-8).
- If the Mn content in the depleted zone is kept constant but its thickness is increased, the simulations reveal that the interface is slowed down for a longer time. Since the Mn depletion is the same for all simulations, the mobility of the interface in the depleted zone should be the same for all simulations as well. Hence, one could expect a linear relationship between the thickness of the region and the time the interface is...
slowed down. As shown by Figure 4-34 b), this is not the case, due to the fact that the temperatures during the simulations are so high that diffusion of Mn cannot be neglected. The results of the simulations show that with increasing thickness of the Mn depleted zone, the minimum Mn content in the depleted zone, found at the end of the simulation, decreases. For a thickness of 3 µm the minimum Mn content increases from 0.5 Wt. % to 0.58 Wt. %. For a thickness of 1.5 µm the minimum Mn content increases from 0.5 Wt. % to 0.67 Wt. %, which implies that the increase in Mn in the Mn depleted zone is slower for thicker Mn depleted zones. This means that there exist two reasons for the more efficient slowdown of the interface in the thick Mn depleted regions. Besides the fact that the interface has to move a longer way in the depleted zone, the depletion is also stronger.

- The position of the depleted zone in the cell also influences how strongly the interface is slowed down. If the depleted zone is located at the end of the cell (cf. Figure 4-36), much less Mn depletion is needed to stabilize a small ferrite region, compared to the case where the depleted zone is located in the middle of the ferrite (cf. Figure 4-34). In the case of the simulation, where the Mn depleted zone is located at the end of the ferrite region, the used Mn values (1 Wt. %) are much more comparable to the measured Mn values (1.3 Wt. %) than for the simulation in which the Mn depleted zone is located in the middle of the ferrite cell (0.4 Wt. % Mn to 0.5 Wt. % Mn). By comparing the size of the simulated ferrite regions with the regions measured with WDX (cf. Figure 4-11), it gets obvious that after the isothermal part of the heat treatment the simulated ferrite regions are much smaller compared to the measured ones. Even though, the ferrite regions start to grow during quenching and reach sizes (ca. 4µm) which are much more comparable to the sizes of the ferrite islands measured with WDX.

4.3.2. The evolution of enrichments of substitutional elements during the diffusional growth of bcc

In order to understand the evolution of the enrichments caused by the cementite lamellae of the pearlite, some DICTRA simulations were performed, which start at the beginning of the isothermal heat treatment. For all simulations it was supposed that at the beginning the cementite lamellae were completely dissolved and transformed into austenite, but the enrichments of Mn were still present in the matrix. This seemed to be reasonable, since Figure 4-37 shows clearly that already at 765 °C the pearlite islands start to transform to austenite. Additionally, the dilatometer curves showed that at the beginning of the isothermal heat treatment (840 °C) the reaustenization was nearly completed.
Figure 4-37: SE image of P+F heated up to 765 °C and quenched to room temperature.

In Figure 4-39 the starting conditions of a typical simulation are shown. The matrix is completely austenitic. An inactive ferrite region is located on the left hand side. The figure shows a planar geometry and a closed cell. Here, the total length of the cell is 100 nm. The former cementite lamella of 12 nm width is located on the right hand side. For the calculations, Fe, C, Mn and silicon were taken into account. The starting conditions were obtained as follows. Since it was assumed that the reaustenization was nearly completed, the C content was set everywhere equal (0.138 Wt. %). In the former cementite region the Mn content was set to 13.55 Wt. % and the silicon content was set to 0 Wt. %. The rest of the austenite had a Mn content of 0.55 Wt. %. In total, the cell had an average Mn content of 2.0 Wt. %, which is quite similar to the average Mn concentration of the matrix. The size of the whole cell was obtained by measuring the distance between several cementite lamellae and dividing the average value by two. The thickness of the cementite lamella was calculated in two steps. At first the average equilibrium C concentration in pearlite (0.8 Wt. %) was divided by the C concentration of cementite (6.67 Wt. %). This result was multiplied with the thickness of the simulated cell and taken as the thickness of the former cementite. For a total size of 100 nm this delivers a thickness of 12 nm for the cementite lamella. The simulated heat treatment is plotted in Figure 4-38, which shows that the simulation starts at the
beginning of the isothermal part of the heat treatment. The used growth regime is LEP/LENP, which means that the partitioning of the substitutional elements is taken into account.

Figure 4-38: Heat treatment used during the simulation of the evolution of the enrichments caused by cementite lamellae.

Figure 4-39: Start distribution of the alloying elements used to perform the DICTRA calculation, which helps to understand the evolution of the lamella structure found in P+F after complete heat treatment. The whole cell is austenitic.

In Figure 4-40 the distribution of Mn, Si and C is plotted for different temperatures. After the isothermal part of the heat treatment (84 s), the Mn peak is broadened and its height is reduced. The maximum reduces from 13.5 Wt. % to nearly 4 Wt. %. In contrast to t = 0 s, Si is
now enriched at the position of the higher Mn content. The low content of C at the left side of the cell indicates that some ferrite has already formed. 50 seconds later, the Mn peak decreased to approximately 3.5 Wt. %. The ferrite region has grown already 60 nm and at the growth front between ferrite and austenite a small Mn peak is visible. It indicates that the growth regime changed for PE to LENP. At $t = 141$ s, the height of the Mn peak on the left hand side of the cell is the same as it was at $t = 134$ s. Also the ferrite-austenite interface did not move very far. At $t = 190$ s the distribution of the elements is nearly the same as it was at $t = 141$ s. Only the height of the peak at the growth front is increased. The evolution of the growth front in dependence of the time is plotted in Figure 4-41. It shows that the ferrite starts to grow directly into the austenite. This is due to the fact that the Mn content is so low at the beginning of the simulation that the steel is at this temperature in the two phase region of ferrite and austenite. This means for the real material that if regions with such a low Mn content would be present in the matrix, they would not transform into austenite during heating up. Even though the temperature is constant up to $t = 84$ s, the interface changes its direction of growth between $t = 30$ s and $t = 40$ s. This is due to the broadening of Mn. It increases the Mn content on the left hand side of the cell and helps to stabilize the austenite. The diagram shows additionally that the diffusional growth of the ferrite stops at $t = 141$ s. After this time, the plot does not show movement of the interface any more.
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Figure 4-40: Simulation of the evolution of the distribution of the alloying elements in pearlite during heat treatment. The simulation was performed with DICTRA.

Figure 4-41: Position of the interface in dependence of the time (cf. Figure 4-38). The results are from the DICTRA simulation with the start condition described in Figure 4-38 and Figure 4-39.

In order to understand the influence of the lamella thickness and the spacing between the lamellae, DICTRA simulations were performed for 5 different values of the cementite lamella...
thickness before heat treatment. Since it was fixed that always 12% of the simulated cell belong to the former cementite region, the size of the cell increased with bigger thickness of the former cementite. The results of the simulations are plotted in Figure 4-42. Figure 4-42-a) shows the minimum and the maximum Mn value at the end of the simulation. The minimum value was obtained at the left end of the cell and the maximum value was measured at the right end of the cell. It is obvious that with increasing lamella thickness, the maximum Mn value increases and the minimum value decreases. The plot does not show a strictly linear relation between the lamella thickness and the maximum and minimum.

Figure 4-42-b) relates the thickness of the cementite lamella with the thickness of the austenite region at the end of the simulation. It shows clearly that with increasing thickness of the cementite lamella, the thickness of the austenite region increases. Obviously, the relation between both values is not linear.

Figure 4-42: a) shows the maximum and the minimum Mn concentration at the end of the simulation in dependence on the thickness of cementite. b) shows the thickness of the austenite region at the end of the simulation in dependence on the thickness of cementite.

Summarizing it can be said that in accordance with the experiments, the simulations show the austenite-stabilizing effect of Mn enrichments. The experimentally measured Mn values lie between 1.7 Wt. % and 2.8 Wt. % and the thickness of the analyzed lamellae is 70 nm ± 18 nm. The standard deviation was chosen as the error. If only the measured thickness of the austenite lamellae is taken into account, the simulations reveal for the start thickness of the cementite lamella a value lying between 20.4 nm and 24 nm. If only the distribution of the Mn is taken into account, the thickness lies between 16.8 and 20.4 nm. Taking into account that only an average value for the Mn content in the cementite was considered, the simulated thicknesses of the lamellae correspond quite well with the measured thicknesses.
4.4. **Conclusion of laboratory-processed material**

The present chapter shows the importance of the initial distribution and diffusion of substitutional elements for the formation of DP microstructures during their heat treatment process.

- The coiling temperature may drastically influence the enrichment of carbides with substitutional elements. High coiling temperatures lead to a high degree of enrichment with substitutional elements like Mn and Cr and promote the formation of Mn depleted regions. Material coiled at low temperatures doesn't contain any enriched carbides. With respect to substitutional elements, the carbides have the same composition as the surrounding matrix.

- During heating up and the isothermal holding, Mn-depleted zones retard the transformation of ferrite to austenite. Since the P+F microstructure contains Mn-depleted zones, it does not austenize completely during the applied heat treatment. With DICTRA it was possible to show the retarding effect of Mn depleted zones on the phase transformation from ferrite to austenite occurring during heating up and the isothermal part of the heat treatment. Additional heat treatments revealed that the ferrite regions are only kinetically stabilized and that an increased plateau temperatures leads to a complete reaustenization.

- During cooling down, the B+M structure transforms at lower temperatures from austenite to ferrite than P+F. The reason for this is that nucleation is needed in the case of B+M. For P+F no nucleation of ferrite is necessary, due to the incomplete austenization of the material. The later transformation of B+M leads to a higher martensite content as well as a higher density of geometrically necessary dislocations, whereby both cause the higher hardness of B+M.

- During isothermal holding the carbides dissolve but the related Mn-enrichments do not homogenize completely. After complete heat treatment, there is a higher chance to find retained austenite at regions of higher Mn content. This does not only happen at former globular carbides but also at former pearlite islands. The microstructure thus resembles the original pearlite but the former cementite lamellae now consist of austenite or martensite. DICTRA calculations show the austenite stabilizing effect of Mn enrichments during cooling down. They show furthermore that Si homogenizes fast enough to prevent the formation of fresh cementite.
5. Analysis of the commercial DP1000

In this chapter the results of the commercially-processed DP1000 produced by ThyssenKrupp Steel Europe AG in a steel plant will be presented. Employing different techniques it will be shown how the microstructure and the mechanical properties evolve. At the end of this chapter, the results will be discussed and compared with the laboratory-processed material.

5.1. Experimental Results

The DP1000 is a low alloyed dual phase steel. Both variants, B+M as well as P+F have the same average composition, which is given in Table 7. The different starting microstructures were tuned-in by different coiling temperatures. In contrast to the laboratory-processed material, the specimens were cold rolled after coiling. The samples were taken from the middle of the band. This applies to the band length as well as to the band width. For all experiments, the specimens were cut in longitudinal section.

<table>
<thead>
<tr>
<th>C (wt. %)</th>
<th>Mn (Wt. %)</th>
<th>Cr (Wt. %)</th>
<th>Si (Wt. %)</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.16</td>
<td>1.89</td>
<td>0.44</td>
<td>0.34</td>
<td>Balanced</td>
</tr>
</tbody>
</table>

Table 7: Average composition of the DP1000

The applied heat treatment, performed in a commercial steel plant, is sketched in Figure 5-1. Here, the plateau temperature was 840 °C. The phase diagram of the material can be seen in Figure 5-2. It reveals that the plateau temperature of the heat treatment is in the pure austenite region. At Point 1 and 2 the heat treatment was interrupted and the microstructure was analysed by using OM. After complete heat treatment (Point 3) SEM, EBSD and WDX have been used to analyse the material. Hardness measurements were applied at all 3 points of the heat treatment. The hardness measurements and microstructure observations were performed in the inner third of the specimen with respect to the thickness.
5. Analysis of the commercial DP1000

Figure 5-1: Sketch of the heat treatment applied to the cold rolled material. The plateau temperature is in the pure austenite region.

Figure 5-2: Phase diagram of the commercially produced material. The phase diagram is calculated with TC.

5.1.1. Evolution of the microstructure analysed with OM

Figure 5-3 presents OM images of the two different microstructures before heat treatment. As shown in the figure, the P+F variant contains islands of pearlite, a ferrite matrix and single carbides lying in the ferrite. The B+M variant consists of ferrite, martensite, bainite and some pearlite. After an interruption of the heat treatment (Point 2), both microstructures (cf Figure 5-4) are nearly completely martensitic. In both variants there are small areas which look like...
undissolved ferrite. Whether this is really the case or whether these areas correspond to an etching artefact cannot be decided. Figure 5-5 shows the microstructure after complete heat treatment. Both samples consist of martensite islands embedded in a ferrite matrix. In the case of the P+F sample, the martensite islands appear to be organized in a more banded way compared with B+M. After analysing more images, this impression was confirmed.

Figure 5-3: OM image of the DP 1000 before heat treatment. The surface is etched with Nital. The left microstructure is a pearlite + ferrite microstructure. The right one is a mixture of martensite, ferrite bainite and some pearlite.

Figure 5-4: OM image of the DP 1000 quenched after the plateau region. The surface is etched with Nital. The left microstructure is created out of the P+F microstructure. The right one is created out of B+M.
Figure 5-5: OM image of the DP 1000 after complete heat treatment. The surface is etched with Nital. The left microstructure is created out of the P+F microstructure. The right one is created out of B+M.

After complete heat treatment (Point 3), the martensite area fraction of both steel variants was determined by OM. As etching agent a solution of 100 ml water and 10 g sodium disulphite was used. This led to a stronger contrast compared to an etching with Nital. After etching the ferrite regions were light grey and the martensite islands were dark grey. The OM images were analysed by using Image J (Version 1.44). The histogram shows two peaks (cf. Figure 5-6). One is related to the martensite and one to the ferrite. The martensite regions were selected by varying the threshold between the two peaks and checking visually whether the right regions were selected. This was not straight forward, since the boundary between martensite and the ferrite regions was never sharp. It was always possible to find a minimum and a maximum threshold for the martensite content. As shown in Figure 5-7, four different martensite area fractions are obtained from the same microstructure. All measurements cover the same martensite islands but each island has a different size. It is not possible to say which map shows the real martensite area fraction. Half of the difference between the highest and the lowest area fraction was set as the error for all measurements. It is 10 %. For both microstructures 10 images with a magnification of 1000x were taken into account. The martensite area fraction of P+F was (45 ± 10) % and of B+M it was (43 ± 10) %.
Figure 5-6: Measurement procedure to obtain the martensite area fraction of the OM images. The left part of the figure shows the OM images, the right part the corresponding histogram.

Figure 5-7: Example of different martensite contents obtained from the same microstructures. The yellow line surrounds the martensite. a) corresponds to an area fraction of 30 %, b) corresponds to 35 %, c) to 41 % and d) to 49 %.

5.1.2. The development of the hardness

The Vickers hardness was measured at different points of the heat treatment. After cold rolling the P+F variant is softer, compared with the B+M material. This was to be expected since it is known that martensite and bainite harden the material more than pearlite. After
interrupting the heat treatment, both specimens have nearly the same hardness. At the end of the heat treatment the B+M variant is harder again.

![Graph showing hardness development](image)

**Figure 5-8: Development of the hardness of both variants of DP 1000.**

### 5.1.3. Detailed microstructure analysis performed with EBSD, WDX and SEM

In order to find an explanation for the different hardness values of both variants, the microstructure was analysed using EBSD. The large area technique described on page 41 was applied for the measurements. The grain size of ferrite, the GND density, and the martensite content were determined. For the P+F microstructure, 80 maps with an edge length of about 20 µm were obtained. The total size of the measured maps covered a rectangle of 364.95 µm x 72.23 µm and was distributed on a rectangle of 1300 µm in x direction and 770 µm in y direction. 9513 ferrite grains were analysed to determine the GND density and the average grain size. For B+M the size of the small maps was the same as for P+F. 64 maps were measured here in total. They covered a rectangle of 646.3 µm x 40 µm and were distributed over a rectangle of 7750 µm x 330 µm. The bcc-iron was separated into ferrite and martensite. 7213 ferrite grains were analysed to determine the GND density and the average grain size. The GND density was calculated in the same ways as for the laboratory-processed material. The results of the measurements can be found in Table 8. It shows that the B+M microstructure has a higher martensite content compared to P+F. The average GND density is higher as well. This is not only the case for the total bcc-iron (martensite and ferrite) fraction but also for the pure ferrite. The grain size of B+M is slightly smaller compared to P+F. These results are comparable to the laboratory-processed material.
DP 1000 | Ferrite grain avg. diameter (µm) | Martensite area fraction (%) | bcc-iron average GND density \( \left( \frac{1}{m^2} \right) \) | Ferrite average GND density \( \left( \frac{1}{m^2} \right) \)  
---|---|---|---|---
P+F | 2.59 | 15.9 ± 1.9 | \( 3.73 \cdot 10^{14} \pm 0.4 \cdot 10^{14} \) | \( 2.98 \cdot 10^{14} \pm 0.3 \cdot 10^{14} \)  
B+M | 2.49 | 21.3 ± 1.2 | \( 4.53 \cdot 10^{14} \pm 0.1 \cdot 10^{14} \) | \( 3.63 \cdot 10^{14} \pm 0.2 \cdot 10^{14} \)  

Table 8: Results of the large area EBSD measurements. DP 1000 P+F and DP 1000 B+M were analysed.

The large area scan of B+M had more points with a low CI compared to P+F. By highlighting all points with a CI < 0.1, it was checked whether all of them were located in martensite. As shown in Figure 5-9, not all points are located in martensite but some are located in a ferrite grain or at the boundary of two ferrite grains. To estimate the amount of points which are not located in martensite, a small map of the large area scan was analysed (cf. Figure 5-9). In total, 3287 points had a CI < 0.1. This is 6.9 % of the total amount of measured points. 282 points lie on the boundary of ferrite or in a ferrite grain. These are 8.58 % of the points having a CI < 0.1 and 0.59 % of the total amount of points. Since this is a small value compared to the total area fraction of martensite (21.3 % for B+M), all points with a CI < 0.1 were counted as martensite.

![Figure 5-9: IQ map of one small scan of the large area scan of P+F. Both maps show the points which have a CI (confidence index) < 0.1. In b) all points with a CI < 0.1 and lying in ferrite grains or at grain boundaries are marked.](image)

Similar to the laboratory-processed material the P+F variant contained ferrite grains with a quite low GND density and grains with a quite high GND density. For B+M only grains with a quite high GND density were found (cf. Figure 5-10).
5. Analysis of the commercial DP1000

Figure 5-10: GND density distribution of the commercially-processed material. a) shows the GND density map of P+F. b) shows the GND density map of B+M. The step size of the map is 100 nm and the 2nd neighbour KAM was used for the plot.

Figure 5-11 shows the distribution of C and Mn after complete heat treatment for B+M. The Mn is not distributed homogeneously. It is enriched in a banded structure where it varies between 1.6 and 2.6 wt. %. The C is enriched in the form of islands. This is quite similar to the distribution of martensite in P+F. The C rich regions follow the distribution of Mn. At the position of high Mn bands the C rich phases can be found more often. In the case of P+F the distribution of the elements is slightly different. Figure 5-12 shows the more inhomogeneous distribution of Mn typical of P+F. Besides the band-shaped enrichments of Mn, several small Mn enrichments can be found, which seem to correlate with the high C zones. In order to check this correlation, the Mn and C signal images were overlaid using Photoshop (Version 5.5). The high Mn zones were marked with a counting tool. Afterwards the Mn layer was hidden and it was checked whether the marks were positioned inside high C zones. 100 points were checked for P+F. 98% of the high Mn zones correlated with the high C zone. Additionally it looks as if the high C zones present in P+F are smaller, compared to B+M.
Figure 5-11: Distribution of C and Mn for B+M after complete heat treatment. The maps were measured with WDX. The step size was 300 nm. The dwell time was 500 ms and the beam current was 40 nA.
Figure 5-12: Distribution of C and Mn for P+F after complete heat treatment. The maps were measured with WDX. The step size was 300 nm. The dwell time was 500 ms and the beam current was 40 nA.
5.1.4. Analysis of the carbides after complete heat treatment (extraction replicas)

To check the distribution and the kind of carbides present in both variants, extraction replicas were created after complete heat treatment. They were analysed by using SEM and STEM. Compared to the martensite, the ferrite was etched more deeply and therefore had a rougher surface. The carbides were identified using EBSD and EDX according to the method described on page 43. In both microstructures Ti carbonitrides and Fe carbides were found. The Fe carbides were always surrounded by martensite or retained austenite. Both, martensite and austenite cannot be distinguished by analysing the extraction replicas. In the case of the P+F microstructure two different kinds of Fe carbides were verified, cementite and M23C6. In the case of B+M only cementite was discovered. Ti carbonitrides were found in martensite as well as in ferrite. The area fraction of Fe carbides determined with large area EDX measurements was $4 \cdot 10^{-4}$ for P+F and $4.8 \cdot 10^{-5}$ for B+M. Therefore, the P+F microstructure has nearly 10 times more carbides compared to B+M. To obtain an impression of the enrichments of Fe carbides with substutional elements, EDX spectra were measured. This was done for the P+F microstructure as well as for the B+M microstructure. In the case of the B+M microstructure, the Fe carbides did not show any enrichment. In the case of the P+F microstructure the Fe carbides were enriched with substutional elements. For Mn and Cr values up to 18 wt.% were found, which is comparable to the values found for the laboratory-processed material. The found enrichments are much higher than the average concentration values.

Figure 5-13: SEM-STEM image of the P+F microstructure. Since it is an extraction replica, it shows the differences in heights vice versa as to what they are in reality.

5.2. Discussion and Conclusion

The discussion of the experimental results is divided into two parts. First, the different martensite area fractions measured with EBSD and OM will be discussed. Afterwards the
results of the analyses performed on the DP1000 will be discussed and compared with the laboratory-processed material.

As already pointed out in Chapter 5.1.1, the martensite area fractions obtained by OM have a huge margin of error which means that the relative error is nearly 25%. The influence of the magnification of the microscope and the size of the analysed features on the margin of error was discussed in ([100] p. 61). As expected, the authors found that for smaller features higher magnifications are needed to obtain reliable results. For a magnification of 1000 X and a feature size of 1 μm they found a relative error of 15 %, which is lower than the error found in the present study.

The martensite area fractions measured with EBSD are much lower compared to the values measured with LM. For P+F, EBSD measurements revealed a martensite area fraction of 15.9 % ± 1.9 %. This is only about a third of the value obtained by OM (45 % ± 10 %). For B+M, the area fraction obtained by OM (43 % ± 10 %) is still twice as large as the area fraction obtained by EBSD (21.3 % ± 1.2 %). The errors of the EBSD measurements are also much smaller. This is very important if one wants to relate measured martensite contents to the mechanical properties of the material. If only the results of the OM measurements were taken into account, both steel variants would have the same martensite content, which would mean that the martensite content would not be an explanation for the different hardness values. In contrast, EBSD measurements show a difference in the martensite content, which correlates with the different measured hardness of the material.

In order to make a comparison with the laboratory-processed material possible, only the martensite area fractions measured with EBSD were taken into account. In terms of hardness, the commercial material has the superior properties compared to the laboratory-processed steel. This applies for B+M as well as for P+F. Comparing the properties of B+M and P+F for the commercial and the laboratory-processed material, it becomes obvious that the commercial steel and the laboratory-processed steel follow the same trend. In both cases the B+M variant is harder, shows a higher average GND density in ferrite as well as in the total bcc-iron fraction, contains a higher martensite area fraction and has a more homogeneous distribution of Mn than the P+F material. This means that for the commercial material the same conclusions can be drawn as for the laboratory-processed material, which implies that the inhomogeneous distribution of Mn caused by the Fe rich carbides is the main reason for the growth of bcc at higher temperatures for P+F in comparison with B+M. This leads to the lower hardness of P+F compared to B+M.
6. GNDs in ferrite formed at different temperatures

In the last two chapters it was shown that the GND density in ferrite is related to the formation temperature of ferrite. If all ferrite is formed at 510 °C (B+M) the average GND density in ferrite is higher than in the ferrite which grew between 668 °C and 510 °C (P+F). Additionally the distribution of the GNDs in ferrite was found to be related to the formation temperature. In ferrite which starts to grow at higher temperatures, high GND regions were found as well as low GND regions. Since continuous cooling was applied it was not possible to correlate the different GND values with a certain formation temperature of ferrite. In this section it will be shown more systematically, how the growth temperature of ferrite influences its GND density. In order to do so, the laboratory-processed B+M variant was reaustenized and subsequently quenched to different temperatures, at which the material was isothermally annealed and ferrite started to grow. Afterwards the material was quenched to room temperature and analysed with EBSD, hardness measurements and ECCL. The results of these analyses will be presented in the following. At the end of this chapter, the results will be discussed and compared with the findings of Chapter 5 and 6.

6.1. Experimental results

6.1.1. Results of the dilatometer experiments

From the dilatometer experiments performed in Chapter 4.1.1, it can be concluded that the austenite created in B+M during the reaustenization can be undercooled at least down to 510 °C, if cooling is fast enough. This means that the B+M variant is perfectly suitable to produce ferrite at different temperatures. In total, 5 specimens were annealed at different temperatures. The results of the dilatometer experiments are presented in Figure 6-1, whereby the same dilatometer was used as for the heat treatments applied in Chapter 4. As can be seen from Figure 6-1 a), the highest temperature for the formation of ferrite was 650 °C and the lowest 450 °C. By using diagrams similar to Figure 6-1 b) it was checked whether in all cases the formation of ferrite starts at the desired temperature. From this type of figures it got obvious that for all temperatures including the lowest as well as the highest the formation of ferrite starts with the beginning of the second isothermal holding.
6. GNDs in ferrite formed at different temperatures

Figure 6-1: Results of the dilatometer experiments applied to the material. a) shows the heat treatment and b) shows the length change of two specimens in dependence of the time.

6.1.2. Development of the hardness

After complete heat treatment, the hardness of all specimens, except for the one annealed at 450 °C, was measured according to the method described in Chapter 3.2. The results of the measurement are presented in Figure 6-2. The lowest hardness is found at a temperature of 650 °C and the highest is found at a temperature of 575 °C. At temperatures lower than 575 °C the hardness decreases slowly.

Figure 6-2: Hardness of the specimens annealed at different temperatures.
6.1.3. **Evolution of the GND density in ferrite**

After complete heat treatment, EBSD measurements were applied to all specimens. The size of the map (95 µm x 150 µm) and the step size (100 nm) was the same for all measurements. In order to calculate the GND densities, the method described in Chapter 3.4.3.2 was used. Figure 6-3 presents the results of the EBSD map measured on the specimen annealed at 575 °C. In the IQ map, martensite and ferrite can be separated by the grain average IQ. The brighter grains belong to ferrite and the darker ones to martensite. The GND map (cf. Figure 6-3 b) shows clearly that the martensite regions have a higher GND density than the ferrite regions. In the ferrite itself, the GND density is not distributed homogeneously. Higher GND density values are organized in a network-like structure. The results of the EBSD measurement performed on the specimen annealed at 600 °C are shown in Figure 6-4. Here, ferrite and martensite can be separated the same way as for Figure 6-3. Again, the martensite areas show higher GND density values than the ferrite regions. Comparing the ferrite regions between the specimen annealed at 575 °C and the specimen annealed at 600 °C in terms of the GND density, one can see clearly that the ferrite formed at 600 °C seems to have a lower GND density than the ferrite formed at 575 °C. Additionally, the network-like structure of the GND density in ferrite is less pronounced in the specimen annealed at 600 °C. Further EBSD measurements showed that at 650 °C the ferrite looked similar to the ferrite found in the specimen annealed at 600 °C. In the specimens annealed at 550 °C and at 500 °C, the ferrite appeared similar to that in the specimen annealed at 575 °C.

![Figure 6-3: Microstructure of B+M annealed at 575 °C and analysed with EBSD. a) shows the IQ-map of the microstructure. The brighter regions are ferrite and the darker ones are martensite. a) presents the GND density map of the same microstructure. The 2nd neighbour KAM was used for plotting the GND densities.](image-url)
6. GNDs in ferrite formed at different temperatures

Figure 6-4: Microstructure of B+M annealed at 600 °C and analysed with EBSD. a) shows the IQ-map of the microstructure. The brighter regions are ferrite and the darker are martensite. a) shows the GND density map of the same microstructure. The 2nd neighbour KAM was used for plotting the GND densities.

In contrast to the other specimens, the microstructure annealed at 450 °C has a completely different shape of the ferrite grains. Here, a lot of the ferrite grains look like a typical bainite microstructure (cf. Figure 6-5) with nearly no martensite in the matrix. Due to the nature of the microstructure most of the ferrite grains are lath-shaped and their GND density is quite high. Even though, there still exist some ferrite grains, which are equiaxed.

Figure 6-5 Microstructure of B+M annealed at 450 °C and analysed with EBSD. a) shows the IQ-map of the microstructure. The brighter regions are ferrite and the darker are martensite. a) shows the GND density map of the same microstructure. The 2nd neighbour KAM was used for plotting the GND densities.
In order to compare the GND density in a more quantitative manner, the average GND density of ferrite was calculated. Therefore, the following procedure was applied. At first, the martensite regions were separated from the ferrite using the method described in Chapter 3.4.3. This was followed by excluding the grain boundaries and their directly neighbouring regions from ferrite grains. To do so, the 3rd KAM value was calculated for ferrite up to a misorientation of 65 ° which creates a KAM map in which also the high angle grain boundaries appear, but they show high KAM values. Subsequently, all KAM values higher than 10° were highlighted and counted as boundary points. A threshold of 10° was chosen, since for this value the boundaries and their direct surrounding were highlighted successfully. Examples for the maps created with this procedure are shown in Figure 6-6. One can see clearly that only the pure ferrite grains are taken into account but no grain boundaries and their direct surroundings and no martensite grains. The results of the EBSD measurements performed on the different specimens are summarized in Figure 6-7. It is apparent from this figure that the average GND density in ferrite decreases with decreasing temperature. This counts for the case where the points near the grain boundary are excluded as well as for the case where they are taken into account. Between 575 °C and 600 °C the average GND density drops significantly faster with decreasing temperature than between 575 °C and 550 °C or between 650 °C and 600 °C. The martensite content varies as well with decreasing temperature. Between 650 °C and 575°C it is about 30 %. When lowering the temperature it reaches values of 20% at 500 and of only 5% at 450°C. (cf. left hand side of Figure 6-7).

![GND density maps of ferrite created at different temperatures. The dark zones mark the ferrite boundaries and the martensite region. The 2nd neighbour KAM was used for plotting the GND densities.](image-url)
6. GNDs in ferrite formed at different temperatures

Figure 6-7: Results of the EBSD analysis performed on the ferrite created at different temperatures. On the left hand side the GND density of ferrite is plotted. On the right hand side the martensite area fraction is shown.

6.1.4. Measuring the grain size

For the strength of a material it is not the grain size which matters but the density of boundaries, even though both are in most cases related to each other. Measuring the grain size in a conventional way, for example with EBSD, has the disadvantage that only those grain boundaries are taken into account, which completely surround a grain while all others are neglected. By measuring the grain boundary density \( \rho_{gb} \) with EBSD, all grain boundaries are taken into account. The grain boundary density is defined as follows:

\[
\rho_{gb} = \frac{A_{EBSD}}{x_{gb\, total}},
\]

whereby \( A_{EBSD} \) is the measured area of an EBSD measurement and \( x_{gb\, total} \) is the total length of the grain boundaries.

Since the strengthening caused by grain boundaries is most times calculated with the Hall-Petch relation, which uses the grain diameter, it is reasonable to calculate an equivalent grain size. This can be done under the assumption that all grain boundaries are distributed homogeneously in the material and that all grain boundaries are distributed on a square grid (cf. Figure 6-8). The total length of the grain boundaries as well as \( A_{EBSD} \) are then defined as following:

\[
x_{gb\, total} = d_{gb} \cdot 2(n + 1) \cdot n
\]

\[
A_{EBSD} = (n \cdot d_{gb})^2
\]

Here \( d_{gb} \) is the equivalent grain size and \( n \) is the number of the grains in x direction. Combining (6.1) with (6.2) and (6.3) leads to:
\[
\rho_{gb} = \frac{A_{FEBSD}}{x_{gb\text{ tot}}} = \frac{2(n + 1)}{n \cdot d_{gb}} \tag{6.4}
\]

If the measured map is much bigger than the grain size, (6.4) simplifies to:

\[
\rho_{gb} \approx \frac{2}{d_{gb}} \tag{6.5}
\]

Figure 6-9 a) presents the grain boundary density in ferrite in dependence on the temperature. Down to 500 °C the high angle grain boundary density does not change much with decreasing temperature. In contrast, the low angle grain boundary density (4°-15 °) increases very much between 600 °C and 575 °C. At 450 °C the high angle grain boundary density is much higher than at the other temperatures. Figure 6-9 b) compares the equivalent grain size with the grain size measured with OIM Analysis (version 6.2). In the case that all grain boundaries larger than 4° are taken into account the equivalent grain size calculation results, for all temperatures except 550° C, in a smaller grain size than the grain size measured by OIM, even if all grain boundaries larger than 1° are taken into account. Generally, the grain size calculated by OIM is increasing with increasing grain tolerance angle. The equivalent grain size was not calculated for the sample annealed at 450 °C.

Figure 6-8: Explanation for the calculation of the equivalent grain size. The red lines show the grain boundaries.
6. GNDs in ferrite formed at different temperatures

Figure 6-9: Grain boundary density and grain size of ferrite formed at different temperatures. a) presents the grain boundary density in dependence on the temperature. b) shows the grain size for different tolerance angles and the equivalent grain size. For the equivalent grain size, all grain boundaries with a misorientation between 4°-180° were taken into account.

6.1.5. Results of ECCI combined with EBSD

In order to analyse the ferrite with the high average GND density and the ferrite with the low average GND density in more detail, ECC images were obtained from the regions which have already been analysed with EBSD to measure the GND densities. In Figure 6-10 the GND density maps are shown together with ECCI images. In the lower right part of the Figure one can see in the ECC image a dislocation line which goes from the light grey region into the black part, which is in Bragg contrast. At the same position the GND density map shows a high dislocation density, which corresponds to a high misorientation. In the dark parts of the ECC images one can see additionally a lot of individual dislocations (named here “statistically stored dislocations” SSD), which do not lead to a change in the crystal orientation measureable with EBSD and therefore are not taken into account during the calculation of the GND density (For more images see the appendix). A comparison of ECC images created from the ferrite annealed at different temperatures (cf. Figure 6-11) suggests that the microstructure annealed at 575 °C has a higher SSD density than the microstructure annealed at 600 °C and 650 °C. In Figure 6-11 the microstructure annealed at 650 °C seems to have a higher SSD density than the microstructure annealed at 600 °C.
Figure 6-10: ECCI and GND measurements performed at the same positions at a sample annealed at 575 °C.
Figure 6-11: Comparison of ECC images measured at different temperatures.
6.2. **Discussion of the results**

In order to make a decent discussion possible, a short summary of the results will be given.

- The B+M microstructure was reaustenized completely and undercooled to different temperatures. At these temperatures the ferrite started to grow into the austenite. After 400 seconds the specimen was quenched to room temperature and the still existing austenite transformed into martensite. After this heat treatment, all microstructures looked like a typical dual-phase steel structure.

- After excluding martensite from the bcc-iron fraction, the GND density was calculated for the ferrite grains by the use of EBSD mappings. The GND density increased with decreasing temperature. Between 600 °C and 575 °C a particularly strong increase occurred.

- The equivalent grain size decreased quite strongly between 575 °C and 600 °C. Between 650 °C and 600 °C as well as between 575 °C and 500 °C it did not change very much.

- The shape of the ferrite grains did not change very much between 575 °C and 600 °C. However, the ferrite grains formed at 575 °C and lower appeared more irregular shaped than the ferrite grains formed at higher temperatures. At 450 °C a bainitic microstructure is present mixed with some equiaxed ferrite grains.

- ECC images suggested that the ferrite formed at lower temperature contains more SSDs than the ferrite formed at higher temperatures.

- With decreasing formation temperature of ferrite, the hardness of the material increased and reached a maximum at 575 °C. A further decrease of temperatures led to again decreasing hardness values.

6.2.1. **The development of the hardness**

In order to understand the development of the hardness in dependence of temperature, the martensite volume fraction, the martensite C content, the GND density and the grain boundary density has to be taken into account. The highest hardness is found at 575 °C, since here the martensite volume fraction is the highest as well as the average GND density in ferrite shows quite high values and additionally the low angle grain boundary density in ferrite is increased significantly. For higher temperatures, the martensite content stays on a high level but the average GND density and the low angle grain boundary density decreases. For formation temperatures lower than 575 °C the average GND density as well as the low angle grain boundary density increase but the martensite content decreases, which could be an explanation for the decreasing hardness values for lower temperatures.
To address the influence of the different parameters of the microstructure on the hardness of the steel in a more quantitative way, the following assumptions were made.

- The total hardness is a mixture of the hardness of the martensite and the hardness of the ferrite. Both determine the overall hardness equivalent to their volume fraction.

\[ \text{Hardness}_{\text{total}} = x_M \cdot \text{Hardness}_M + x_F \cdot \text{Hardness}_F \]

With \( x_M \) and \( x_F \) being the volume fraction of martensite and ferrite.

- The hardness of martensite can be calculated using

\[ \text{Hardness}_M = \left(28 + 2323(c(C)) - 1143(c(C))^2 - 833(c(C))^3\right) \text{HV} \]

Whereby the concentration of \( C \) (\( c(C) \)) can be derived by dividing the overall \( C \) concentration in the material by the volume fraction of martensite, assuming that all carbon is dissolved in martensite.

- In order to calculate the hardness of the ferrite the Hall-Petch relationship as well as the work hardening caused by dislocations can be used.

- The Hall-Petch relation can be formulated as follows

\[ \sigma_d = \sigma_0 + \frac{k_y}{\sqrt{d}} \]

Whereby \( d \) is the average diameter of the ferrite grains, \( \sigma_d \) is the yield stress caused by the grain diameter, \( \sigma_0 \) is a materials constant for the stress needed to cause dislocation movement (70 MPa) and \( k_y \) is the strengthening coefficient (0.75).

- The work hardening caused by dislocations can be calculated using a Taylor equation.

\[ \sigma_T = \alpha G b \sqrt{\rho_D} \]

Here \( \alpha \) is the dislocation strengthening constant (0.5), \( G \) is the shear modulus of Fe (83 GPa), \( b \) is the length of the Burgers vector (2.48 \( \cdot \) 10\(^{-10}\)m) and \( \rho_D \) is the dislocation density in ferrite calculated by the GND measurements.

- The calculated yield strength of the ferrite can be transformed into the Vickers hardness by the following equation:

\[ \text{HV}_{\text{ferrite}} = \frac{\sigma_d + \sigma_T}{3.025} \]

The hardness values calculated with this equation are presented in Figure 6-12. Comparing this with the measured hardness values, it becomes obvious that the calculated values are about 60 HV too high. The hardness calculated for the ferrite grown at 650 °C is even 100 HV to high. Even though, the highest hardness is found as well at 575 °C, similar to the measured hardness. Also the difference between the hardness found at 575 °C and 600 °C is not too different (30 HV for the calculated values and 40 HV for the measured ones). A possible reason for the difference in the hardness of the ferrite formed at 650 °C could be that at this temperature some Fe carbides could have formed. If this would be the case, less C would be available for the martensite and the hardness of the martensite would be lower. If for example the hardness of the specimen annealed at 650 °C should also be only 60 HV higher than the real value, 0.04 Wt. % C should not be dissolved in martensite. What has not been taken into account during the calculation of the hardness is the influence of the SSDs. In order
to calculate the influence of all dislocations on the hardness, the SSD density as well as the GND density should be taken into account. Even though, this would lead to an even higher calculated hardness value.

![Graph](image)

**Figure 6-12: Hardness of the steel calculated by the results of the EBSD measurements.**

### 6.2.2. Grain size vs equivalent grain size

The calculation of the average grain size, here weighted by area, by EBSD has some disadvantages. As shown in Figure 6-9, different values of grain tolerance angle lead to different sizes of the grains. This means, in particular, that with decreasing grain tolerance angle the calculated grain size decreases as well. This is caused by the fact that for low grain tolerance angles more misoriented areas are counted as boundaries. A disadvantage of this technique is that if a grain is not completely encompassed by a boundary, two grains may be regarded as one grain, which increases the grain size dramatically. As already mentioned in Chapter 6.1.4 it is not the grain size, which is responsible for hardening of a material but the grain boundary density, although the Hall Petch relation uses the grain size. The main advantage of calculating the equivalent grain size out of the grain boundary density is that it also includes the grain boundaries which do not surround a whole grain. It cannot happen that two grains are counted as one, just because the boundary between two grains has at one position a too low misorientation and therefore contains a hole. The observation that the equivalent grain size is not always the smallest is related to the fact that in the present study a simple square grid was used for calculating the equivalent grain size. Assuming round
shaped grains would lead to a smaller equivalent grain size, which would probably be smaller than the measured values.

If one wants to calculate the equivalent grain size of ferrite in a martensite ferrite microstructure, the martensite has to be accurately excluded from the analysis. This is due to the fact that the martensite contains a lot of high angle grain boundaries which can lead to a very high total grain boundary density, which, in turn, raises the average grain boundary density dramatically. Here, it is even safer to estimate a too high martensite area fraction, in order to be sure that only ferrite grains are taken into account for the measurement of the grain boundary length.

### 6.2.3. A change in the growth regime of ferrite

Besides the ferrite types described in Chapter 2.4.4, several studies deal with an equiaxed type of ferrite, which forms at lower temperatures than the normal polygonal ferrite \([103]\). In literature this type of ferrite is not named consistently. Granular ferrite \([104]\), quasi-polygonal ferrite \([100, 103]\) and recovered \([100]\) ferrite are some of the used names. In the following we will use the term granular ferrite. In general it is differentiated from polygonal ferrite by its jaggedly formed grain boundaries \([105]\). Thompson et al report that this type can be found in low C low-alloy steels \([104]\). They assume that it grows reconstructively, since the granular shape of the grains is not consistent with a displacive growth mechanism. It was found by Thompson et al. as well that the granular ferrite has a high dislocation density, which is comparable to the dislocation density in acicular ferrite. As a reason they suspect the accommodation of volume change caused by the lower temperature compared to polygonal ferrite. Araki et al. assume two different formation mechanisms for the granular ferrite \([105]\). If the C concentration is very low (0.01 Wt. %), it forms in accordance with a massive phase transformation (diffusional), if the steel has a higher C concentration, it grows in accordance with LENP.

Since in the present study the ferrite formed between 500 °C and 575 °C has an irregular shape, it is very likely that it is also a granular ferrite. The higher GND densities found at lower temperatures are also in accordance with the results reported in literature. Even though, the detailed EBSD analysis supports a different view on the growth regime of the granular ferrite. As will be shown below, it is for a number of reasons very unlikely that the granular ferrite is in principle a polygonal ferrite which just has grown at lower temperatures as reported by Thompson et al \([104]\).

Taking just the shape of the ferrite grains and the large angle grain boundary density into account, the results of this study would suggest that ferrite grown at temperatures higher than 450 °C has formed reconstructively, since all ferrites grown between 500 and 650 °C
have equiaxed grains and a comparable grain boundary density. In contrast, ferrite grown at 450 °C has lath-shaped grains, which is normally related to a displacive growth mechanism [39]. However, the results of the GND measurements do not correlate with changes on the shape of the ferrite grains and grain boundary density values. The strongest change in the ferrite average GND density is found between 600 and 575 °C where the increase in the GND density is even higher than between 575 and 450 °C.

In order to explain the changes in the average GND density with respect to temperature, different factors which could influence the GND density have to be taken into account. In the case of a reconstructive phase transformation, the GNDs can only be introduced into the material by the accommodation of volume change induced by the phase transformation from fcc to bcc [106]. The different atomic density of bcc and fcc leads to strain which is accommodated by randomly arranged dislocations in the ferrite during the growth of bcc. In the case of a displacive phase transformation, GNDs are not only introduced by the volume change of the phase transformation but also by the displacive phase transformation itself. The fixed crystallographic relationship between the bcc and fcc phase during a displacive phase transformation produces a shear strain, which has to be accommodated mainly by the newly formed bcc as well as the neighbouring fcc. As the transformation strain has everywhere in a given crystal the same direction and magnitude it is compensated by dislocations of the same type, i.e. by GNDs. In consequence, this means that a displacive phase transformation should produce more GNDs than a reconstructive one. Following this criteria it can be suggested that the growth regime changes from reconstructive to displacive between 600 °C and 575 °C and not between 500 °C and 450 °C, even though the shape of the ferrite crystals at 575 °C, 550 °C and 500 °C is still equiaxed and not acicular as many ferrite grains are at 450 °C.

In order to understand the change of the shape of the ferrite grains occurring between 500 °C and 450 °C, 2 papers presented by Furuhara et al. are of great worth [107, 108]. Here, the crystallography of upper bainite [108] and the variant selection during the nucleation of upper bainite [107] are discussed. It is known that similar to lath martensite, 24 different variants of bainitic ferrite can grow from the same type of austenite. Except from minor differences, these 24 different variants follow the Kurdjumov-Sachs orient relationship (cf. Chapter 2.4.3). Thereby, it depends on the driving force, which and how many variants of bainitic ferrite growths from the former austenite. For low driving forces (low undercooling), only 1 or 2 variants start to grow from the same boundary and the variants are separated by small angle grain boundaries. In the case of such a growth mechanism, the authors found very large regions (several 10^6 of µm in diameter), which had the same orientation. For higher driving forces (higher undercooling) they discovered that more variants can grow from the
same austenite boundary. As a reason the authors assumed that for high driving forces the difference in the nucleation energy between the different bainitic ferrite variants play a smaller role than for lower driving forces. As a consequence, more variants can start to form, which grow in the form of single laths which are separated by large angle grain boundaries. Additionally, the self-accommodation of strain is increased due to the growth of different bainitic ferrite variants. This is important since at lower temperatures (high driving force) it is difficult to transform the neighbouring ferrite or austenite plastically. In the present study it could be the case that between 575 °C and 500 °C the driving force is not high enough to allow different variants of bainitic ferrite to grow from the same austenite and therefore the entire austenite grain transforms the same way. At 450 °C the driving force could be high enough to allow different variants of bainitic ferrite to grow and the bainitic ferrite starts to grow in the form of single laths.

With the intention of explaining the observed increase in the average GND density in ferrite between 575 °C and 450 °C, Figure 6-13 is presented. It is clear that for a temperature of 575 °C most of the ferrite regions have quite a high GND density (green) but there exist still some regions with a lower GND density (blue). The amount of the low GND regions decreases with decreasing temperature which may be explained by the fact that at 575 °C not all austenite regions can transform displacively into bcc due to inhomogeneous stress distribution in the material. It is known that in general displacive phase transformations are retarded by plastic deformation which is called mechanical stabilisation [109]. In contrast, elastic strain promotes the displacive transformation. For lower temperatures the driving force of the phase transformation increases and a displacive phase transformation can also occur in regions which were not able to transform displacively at higher temperatures. This would then increase also the average GND density in ferrite. A mixed growth regime for granular ferrite has been presented by Kang et al [110]. In their work, a low alloy steel (Fe-2.0Mn-0.15Si-0.05C (wt. %)) was reaustenized and subsequently cooled down to room temperature, whereby different cooling speeds were used. For a cooling speed of about 10 K/s they found granular ferrite, which they call granular bainite, however. They suppose a displacive nucleation of the granular bainite and a mixed type of growth (displacive and reconstructive). Even though, a detailed description of the growth mechanism itself is not given in their paper.
6.3. Comparison with the preliminary results

Comparing the results obtained in this chapter with the results obtained in chapter 4 and 5, it becomes obvious that the different GND density observed for B+M and P+F are caused by a change in the growth regime. By means of the dilatometer experiments (cf. Figure 4-3) it was shown that in the case of P+F ferrite started to grow at significantly higher temperatures ($668^\circ C \pm 8^\circ C$) than in the case of B+M ($510^\circ C \pm 1$). Additionally the dilatometer experiments revealed that in the case of P+F, ferrite grew all the time between $668^\circ C$ and $510^\circ C$. Since it was proven that ferrite formed at temperatures higher than $600^\circ C$ has a much lower GND density than that formed below $575^\circ C$, one can conclude that in the case of P+F high GND density ferrite has formed as well as low GND density ferrite. In contrast, B+M contained only high GND density ferrite, due to the lower growth temperature of ferrite.

In Figure 6-14 the average GND density of the ferrite found in the B+M variant is compared with the GND densities found in the present chapter. The average GND density of the B+M
variant is plotted at 510 °C since the dilatometer experiments showed that the ferrite is created at this temperature. It is obvious, that the average GND density of B+M fits very well to the average GND densities of ferrite measured in this chapter.

![Graph showing GND density comparison](image)

**Figure 6-14:** Comparison between the GND density of ferrite produced during the creation of the laboratory-processed material and the GND density of ferrite produced for the analysis performed in this chapter.
7. Summary and outlook

7.1. Summary

- It was shown for commercially-processed material as well as for in lab processed steel that the enrichments of substitutional elements caused by different Fe carbides are a fingerprint in the material, which survives short heat treatments at high temperatures (840 °C). With DICTRA calculations it was possible to show, that even very narrow enrichments (thickness of 24 nm) survive the heat treatment.

- On the example of two different microstructures, which differed in the distribution of the substitutional elements, the influence of the distribution of the substitutional elements on the phase transformation occurring during the heat treatment was shown.

- By using WDX mappings it was shown that Mn depleted zones slow down the transformation of ferrite into austenite during heating and isothermal holding. DICTRA calculations derived that the Mn depleted zones stabilize the ferrite regions kinetically.

- During cooling down, this causes a growth of ferrite at higher temperatures because nucleation is not necessary. The ferrite grown at higher temperatures has a lower average GND density than the ferrite grown at lower temperatures. Additionally the martensite content is higher in the material.

- Measurement of the average GND density of ferrite created at different isothermal temperature regimes suggests that the higher average GND density in ferrite grown at lower temperatures (575 °C and lower) may be caused by a change in the growth regime in ferrite from completely reconstructive to more displacive.

- The reason for the higher hardeneses of B+M in comparison to P+F is the higher GND density of B+M as well as its higher martensite content. This applies for the laboratory-processed material (cf. Chapter 4) as well as the material produced by TKS (cf. Chapter 5).

- The influence of the GNDs is described in Chapter 6. The sample annealed at 575 °C and 600 °C had the same martensite content but different average GND concentrations in ferrite. An increase of the average GND density of ferrite from about $1 \cdot 10^{14} \frac{1}{m^2}$ to $2.6 \cdot 10^{14} \frac{1}{m^2}$ led to an increase of the hardness from 283 HV to 321 HV.
7.2. Outlook

7.2.1. Using Mn enrichments to improve the properties of steel

A class of steels, which is expected to profit from the inhomogeneous distribution of Mn caused by cementite, are the Quenching- and Partitioning steels (Q&P). This class consists of a martensite austenite microstructure, where austenite is enriched with C to stabilize it to lower temperatures \([111]\). To do so, a totally austenitized steel is quenched between \(M_S\) and \(M_F\), which leads to a partial transformation of the austenite to martensite \([112]\). In a subsequently performed annealing, the martensite pushes its C into the austenite, which therefore is stabilized. In order to prevent the formation of carbides, silicon and aluminium are added to the alloy \([113]\). To stabilize the austenite even more, one could think about using Mn enrichments, since it is known that Mn has an austenite stabilizing effect (cf. page 13). Mn enrichments could be produced in the same way, as it was done in the study at hand. This implies that the pearlite is formed at such a temperature that the cementite lamellas are enriched with Mn and that the Mn enrichments don’t dissolve completely during reaustenization. With the intention of maximizing the austenite stabilizing effect caused by Mn enriched cementite, the Mn enrichments in cementite have to be as high as possible and during the reaustenization the Mn enrichments should be homogenized as less as possible. Maximizing the Mn content in the cementite lamellas is not a simple task. On the one hand, as presented in Figure 4-26, the equilibrium concentration of Mn in Fe3C increases with lower temperatures. On the other hand Mn enriches only in cementite during the growth of pearlite. If the temperature is too low the formation of pearlite is replaced by the growth of bainite, in which the cementite is not enriched with substitutional Elements (cf. Chapter 4.1.4.). In order to get the highest Mn enrichments, the reaustenization has to be long enough to dissolve pearlite completely but short enough to prevent from homogenization of Mn in the austenite.

In order to perform the necessary analysis, the material can be examined using the experimental and theoretical methods presented in the study at hand.
8. Appendix

8.1. On the accuracy of the calculation of the GND density distributions

As shown in Chapter 3.4.3.2, the GND density is proportional to the KAM values. This means that the accuracy of the KAM values directly influences the accuracy of the GND densities. With the intention of determining the noise level of the KAM measurements, a recrystallized and deformation free ferrite was analysed using EBSD. Except from the step size, which was 500 nm, the same measurement conditions (15 kV, binning 120, theta step size 1°, convolution mask 9x9, JEOL 6500 FE microscope) were used as for the measurements performed on the steels examined in the present thesis. Subsequent to the EBSD mapping, the grain average misorientation was derived from the measured orientation values. An overview of the measurement is presented in Figure 8-1. It is obvious that not all grains have the same KAM value, even though all grains are free of deformation. The mean value of the grain average misorientation is 0.21° ± 0.1°, whereby the error is the standard deviation of grain average misorientation. This value did not depend on the selected neighbour, which means that the grain average misorientation was the same for the 1st, the 2nd, the 3rd and the 4th neighbour. In order to check whether the step size of the measurement influences the background of the KAM maps, a second EBSD measurement was performed on the ferrite. Here, the step size was 100 nm; all other measurement conditions were the same as for the measurement presented in Figure 8-1. An analysis of the measurement derived the same background for the KAM value as for the measurement performed with a step size of 500 nm.
Figure 8-1: Grain average misorientation measured on undeformed and recrystallized ferrite. The step size of the measurement was 500 nm.

Since the GND density is a physical property of the material, it should be independent of the used KAM neighbour, as long as the step size of the EBSD measurement is the same. As can be derived from Equation (3.3) the GND density is linear proportional to the KAM value and ~1/n, whereby n is the number of the neighbour. This implies that, after subtracting the background of a KAM measurement, the average value of a KAM mapping performed by using the 2nd neighbour should be twice as high as the average value of a KAM mapping, which uses the 1st neighbour. Using the 3rd neighbour should deliver a 3 times higher values than using the 1st neighbour. In general it can be formulated as

\[ KAM_{n-avg} = n \cdot KAM_{1-avg}. \]  

(8.1)

Whereby \( KAM_{n-avg} \) is the average KAM value calculated for the \( n \)th neighbour. In Figure 8-2 the KAM value of B+M annealed at 550 °C is plotted in dependence on the KAM neighbour. Even though, there is a linear relationship between the number of the neighbour and the KAM values, Equation (8.1) is not fulfilled. As shown above, the noise of the KAM value is a constant and does not depend on the number of the used neighbour. Taking Equation (8.1) into account, one can derive that the slope of the linear fitting is the real value of \( KAM_{1-avg} \) and the intersection with the y-axis is the background which has to be subtracted from the measurement. For all KAM measurements performed in the study at hand, the background was calculated in such a way and the corrected average KAM values were used to calculate the average GND densities. The error of the average GND density was calculated by using the
error of the slope of the linear fit of the measurement as well as the error of the intersection of the linear fit with the y-axis. In all maps showing GND densities, the background has not been subtracted. Here, the GND densities depend on the raw KAM including the background.

The background of the average KAM value is not the same for every measurement. This is due to the fact that the accuracy of the determination of the KAM value depends on the quality of the EBSD patterns as well as on the measurement conditions, which has been shown by Zaefferer ([114] p.97). In the study at hand it was found that the background of the average KAM values was influenced by the used microscope, the measurement conditions and the analysed phase.

The influence of the used system is shown in Figure 8-4. Here, the average GND densities are shown in dependence on the used KAM value and the used system. For the same KAM value, the Bruker system (Zeiss Merling FEG-SEM equipped with a Quantax EBSD system e-Flash hr and the software Esprit (version 1.9)) shows a higher value than the TSL system (cf. p. 38), even though the quality of the obtained patterns was comparable. This is most likely due to the different indexing process of the both system. Nevertheless, the GND density after background subtraction was for both systems the same.

During the study it was observed that measurements which included large fraction of martensite had a higher background than measurements which only included ferrite. The reason for this is probably the worse pattern quality of martensite compared to ferrite. In consequence this means that if the background (or spurious) GND density is not subtracted from the average GND density, the amount of GND in deformed material is overestimated in comparison with the GND density in undeformed material. The same applies for different phases in which the pattern quality changes.

In Figure 8-3 the average GND densities of ferrite of the steel presented in Chapter 6 are shown. Here, the values after and before background correction are presented. Before background correction, the GND values were calculated using the 2nd KAM value. They are higher if the phase and grain boundaries are included in the measurements. The difference between the values where the boundaries were excluded from the calculation and the values where the boundaries were taken into account was than about \(4 \cdot 10^{13} \frac{1}{m^2}\). After background correction, it does not play a role whether the boundary regions are taken into account or not and the average GND densities are about \(1.5 \cdot 10^{14} \frac{1}{m^2} - 2 \cdot 10^{14} \frac{1}{m^2}\) lower than the values obtained before background correction.
Figure 8-2: Average KAM values of ferrite in B+M annealed at 550°C in dependence on different neighbours. The red line is a linear fitting between the measured points. The KAM values were here obtained without a boundary.

Figure 8-3: GND density obtained in chapter 6 with background correction (left) and without background correction. For the values without background correction the 2nd neighbour KAM value was used.
Figure 8-4: Average GND density of ferrite measured at different system in dependence on the used neighbour for the KAM calculation. The red line shows the average GND density measured after background subtraction.
8.2. The combination of GND measurements and ECCI measurements

Even though it is possible to measure the GND density in a material with EBSD, it is not possible with this technique to observe the SSDs in a material. With ECCI in contrast it is possible to observe the SSDs. In order to compare the results obtained by ECCI and by EBSD with respect to the dislocations, both measurements were performed at the same position on different samples. The samples were in detail B+M annealed at 575 °C and B+M annealed at 600 °C (cf. Chapter 6.1.1). The intention of doing so, is to address the question whether it is possible to find a difference in terms of the SSD density between the material with a high average GND density in ferrite (575 °C and lower) and the material with a low average GND density in ferrite (600 °C and higher).

8.2.1. B+M annealed at 575 °C

On the specimen annealed at 575 °C, 6 different combined ECCI EBSD measurements were performed. The results of the measurement, which are shown in the following figures, point out clearly that the misorientations measured with EBSD correspond with a change of the contrast in the ECCI images. The ECCI images show additionally that in the regions with the same orientation, i.e. the regions which have the same contrast level in the BSE images, a lot of dislocations can be found. These dislocations are often organized in cell like structures.
Figure 8-5: Combined ECCI and GND measurement on B+M annealed at 575 °C. The accelerating voltage for the EBSD measurement was 15 kV. The ECCI images were obtained with an accelerating voltage of 28 kV. a) shows the result of the EBSD measurement. b) and c) show the results of the ECCI measurements. The KAM was calculated up to values of 4°.
Figure 8-6: Combined ECCI and GND measurement on B+M annealed at 575 °C. The accelerating voltage for the EBSD measurement was 15 kV. The ECCI images were obtained with an accelerating voltage of 28 kV. a) shows the result of the EBSD measurement. b) and c) show the results of the ECCI measurements. The KAM was calculated up to values of 4°.
Figure 8-7: Combined ECCI and GND measurement on B+M annealed at 575 °C. The accelerating voltage for the EBSD measurement was 15 kV. The ECCI images were obtained with an accelerating voltage of 28 kV. a) shows the result of the EBSD measurement. b) and c) show the results of the ECCI measurements. The KAM was calculated up to values of 4°.
Figure 8-8: Combined ECCI and GND measurement on B+M annealed at 575 °C. The accelerating voltage for the EBSD measurement was 15 kV. The ECCI images were obtained with an accelerating voltage of 28 kV. a) shows the result of the EBSD measurement. b) and c) show the results of the ECCI measurements. The KAM was calculated up to values of 4°.
Figure 8-9: Combined ECCI and GND measurement on B+M annealed at 575 °C. The accelerating voltage for the EBSD measurement was 15 kV. The ECCI images were obtained with an accelerating voltage of 28 kV. a) shows the result of the EBSD measurement. b) and c) show the results of the ECCI measurements. The KAM was calculated up to values of 4°.
Figure 8-10: Combined ECCI and GND measurement on B+M annealed at 575 °C. The accelerating voltage for the EBSD measurement was 15 kV. The ECCI images were obtained with an accelerating voltage of 28 kV. a) shows the result of the EBSD measurement. b) and c) show the results of the ECCI measurements. The KAM was calculated up to values of 4°.
8.2.2. **B+M annealed at 600 °C**

On the specimen annealed at 600 °C, 4 different combined ECCI EBSD measurements were performed. The results of the measurement, which are shown in the following figures, point out clearly that less misorientations are measurable than on the specimen annealed at 575 °C. The ECCI images show that in the regions with the same orientation, i.e. the regions which have the same contrast level in the BSE images, dislocations can be found.

Figure 8-11: Combined ECCI and GND measurement on B+M annealed at 600 °C. The accelerating voltage for the EBSD measurement was 15 kV. The ECCI images were obtained with an accelerating voltage of 30 kV. The upper left shows the result of the EBSD measurement. The others show the results of the ECCI measurements. The KAM was calculated up to values of 4°.
Figure 8-12: Combined ECCI and GND measurement on B+M annealed at 600 °C. The accelerating voltage for the EBSD measurement was 15 kV. The ECCI images were obtained with an accelerating voltage of 30 kV. The upper left shows the result of the EBSD measurement. The others show the results of the ECCI measurements. The KAM was calculated up to values of 4°.
Figure 8.13: Combined ECCI and GND measurement on B+M annealed at 600 °C. The accelerating voltage for the EBSD measurement was 15 kV. The ECCI images were obtained with an accelerating voltage of 30 kV. The upper left shows the result of the EBSD measurement. The others show the results of the ECCI measurements. The KAM was calculated up to values of 4°.
Figure 8-14: Combined ECCI and GND measurement on B+M annealed at 600 °C. The accelerating voltage for the EBSD measurement was 15 kV. The ECCI images were obtained with an accelerating voltage of 30 kV. The upper left shows the result of the EBSD measurement. The others show the results of the ECCI measurements. The KAM was calculated up to values of 4°.
8.3. Abbreviations

$A_{Fe3C}$  Area fraction of cementite

$D_{k}^{*}$  Interdiffusion coefficient of the element $k$

$L'_{ki}$  Proportional factor which depends on the mobility of the species $k$ and $i$

$N_{\alpha}$  Number of atoms belonging to phase $\alpha$

$V_{M}$  Molar volume

$d_{bcc}$  Constant of the unit cell for bcc-iron

$v_{\alpha}$  Velocity of the phase boundary $\alpha$

$x_{k}$  Concentration of the element $k$

$\mu_{i}$  Chemical potential of the element $i$

$b$  Burgers vector

B+M  Bainite plus martensite microstructure

BCC  Body-centered cubic

c  Concentration

CI  Confidence index (Parameter for the reliability of a solution of an EBSD pattern)

CR  Cold rolling

D  Diffusion constant

EBSD  Electron backscatter diffraction

ECCI  Electron contrast channelling imaging

EDX  Energy-dispersive X-ray spectroscopy

eV  Electron volt

FCC  Face-centered cubic

FEG-SEM  Field-emission gun scanning electron microscope

FIB  Focused ion beam

GNDs  Geometrically necessary dislocations

HR  Hot rolling

HV  Vickers hardness

ICA  Intercritical annealing

IQ  Image quality (Quality of an EBSD pattern)

KAM  Kernel average misorientation

$kV$  Kilo volt

LENP  Local equilibrium with negligible partitioning

LEP  Local equilibrium with partitioning
<table>
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<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>$M_s$</td>
<td>Martensite start temperature</td>
</tr>
<tr>
<td>Nital</td>
<td>Solution of ethanol and nitric acid</td>
</tr>
<tr>
<td>OM</td>
<td>Optical Microscopy</td>
</tr>
<tr>
<td>OPS</td>
<td>Oxide polishing suspension</td>
</tr>
<tr>
<td>P/B</td>
<td>Peak to background</td>
</tr>
<tr>
<td>P+F</td>
<td>Pearlite plus ferrite microstructure</td>
</tr>
<tr>
<td>PE</td>
<td>Paraequilibrium</td>
</tr>
<tr>
<td>ROI</td>
<td>Region of interest</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>SSDs</td>
<td>Statistically stored dislocations</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning transmission electron microscopy</td>
</tr>
<tr>
<td>$t$</td>
<td>Time</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
</tr>
<tr>
<td>TC</td>
<td>Thermo Calc</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>WDX</td>
<td>Wavelength-dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>Wt. %</td>
<td>Weight %</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>$\alpha$-iron</td>
<td>Ferrite</td>
</tr>
<tr>
<td>$\gamma$-iron</td>
<td>Austenite</td>
</tr>
<tr>
<td>$J$</td>
<td>Diffusion flux</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density</td>
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</table>
8.5. Acknowledgements

I am grateful to all the kind people around me whose help and support enabled me to write this thesis; not all of them can be mentioned by name.

I would like to express my sincere gratitude to...

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**Curriculum Vitae**

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**Ausbildung**

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<tr>
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<tr>
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<td>Abschluss: Diplom der Physik mit der Gesamtnote sehr gut</td>
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<tr>
<td>Seit Mai 2011</td>
<td>Promotion am Max-Planck-Institut für Eisenforschung GmbH</td>
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8.7. Zusammenfassung

Um die mechanischen Eigenschaften eines Dualphasenstahls zu verbessern, kommt es darauf an, das Gefüge aus Ferrit und Martensit optimal einzustellen. Um dies zu erreichen, muss sowohl die Auswirkung einer Glühbehandlung als auch der Einfluss der Legierungselemente berücksichtigt werden. Bei den Legierungselementen kommt es nicht nur auf die mittlere sondern auch auf die lokale Zusammensetzung im Stahl an.


Beide Warmbänder wurden mit Hilfe eines Dilatometers der gleichen Wärmebehandlung unterzogen, die sich an dem Herstellungsprozess eines Dualphasenstahls orientiert, wie er bei Thyssenkrupp-Steel Europe durchgeführt wird. Bei diesem Glühprozess wird das Material bei 840 °C reaustenisiert und anschließend auf Raumtemperatur abgekühlt. Im Falle der P+F Mikrostruktur stellte sich heraus, dass die Reaustenitisierung nicht komplett abgeschlossen war. Der Grund dafür waren die an Mangan abgereicherten Regionen, welche das Wachstum des Austenits in dem Ferrit verlangsamen. Beim Abkühlen konnte der vererbte Ferrit daher direkt anfangen zu wachsen. Im Gegensatz dazu war die Reaustenitisierung im Falle der B+M Mikrostruktur komplett abgeschlossen und der Ferrit bildete sich erst bei deutlich tieferen Temperaturen. Infolgedessen wies der Dualphasenstahl, welcher seinen Ursprung in der B+M Mikrostruktur hatte (B+M Dualphasenstahl), einen deutlich höheren Martensitgehalt auf als der Dualphasenstahl, der sich aus der P+F Mikrostruktur bildete (P+F Dualphasenstahl). EBSD Messungen, die im Anschluss an die Wärmebehandlung bei beiden Mikrostrukturen durchgeführt wurden, zeigten für den P+F Dualphasenstahl im Vergleich zu dem B+M Dualphasenstahl eine geringere mittlere geometrisch notwendige Versetzungsdichte (GND-Dichte) im Ferrit. Dabei wies der P+F Dualphasenstahl zum einen Ferritregionen auf, welche
eine ähnlich hohe GND-Dichte hatten wie der Ferrit im B+M Duahlphasenstahl, als auch Ferritregionen, die einen deutlich geringere GND Dichte zeigten.

Anhand weiterer Wärmebehandlungen, bei denen Ferrit ausschließlich isotherm gebildet wurde, konnte gezeigt werden, dass sich die Bildungstemperatur des Ferrits deutlich auf seine GND-Dichte auswirkt. Es stellte sich heraus, dass die mittlere GND-Dichte des Ferrits invers proportional zu seiner Bildungstemperatur ist. Eine sprunghafte Zunahme der GND-Dichte im Ferrit zeigte sich zwischen 600 °C und 575 °C. Zwischen diesen beiden Bildungstemperaturen stieg die GND-Dichte im Ferrit deutlich stärker als zwischen 650 °C und 600 °C oder zwischen 575 °C und 450 °C. Es wird vermutet, dass eine Änderung im Wachstumsmechanismus des Ferrits für die sprunghafte Zunahme der GND-Dichte verantwortlich ist. Für 600 °C und höher wird für den Ferrit ein rekonstruktiver Wachstumsmechanismus angenommen. Bei tiefen Temperaturen scheint der Wachstumsmechanismus einen deutlich displassiven Anteil zu haben. Die Form der Ferritkörner, welche oft mit dem Wachstumsmechanismus des Ferrits in Verbindung gebracht wird, ändert sich hingegen erst zwischen 500 °C und 450 °C. Für 500 °C und höher haben die Ferritkörner eine globulare Gestalt. Bei 450 °C hingegen existieren viele Ferritkörner, die eine nadelförmige Gestalt haben, wie sie typischerweise in Bainit gefunden wird.

Mit den im vorherigen Absatz vorgestellten Ergebnissen ist es auch möglich zu verstehen, warum der P+F Dualphasenstahl eine inhomogene Verteilung der GND-Dichten im Ferrit aufweist. Beim P+F Dualphasenstahl bildete sich der Ferrit sowohl bei hohen (600 °C und höher) als auch bei niedrigeren Temperaturen. Da die GND-Dichte invers proportional zur Bildungstemperatur ist, führt dies zu einer inhomogenen Verteilung der GND-Dichten im Ferrit. Beim B+M Dualphasenstahl bildete sich der komplette Ferrit bei ca. 510 °C, was zu einer homogeneren Verteilung von hohen GND-Dichten führte.

Der Einfluss der Startverteilung des Mangans im Warmband auf den fertigen Dualphasenstahl wurde nicht nur für das im Labor hergestellte Material nachgewiesen, sondern auch im Dualphasenstahl, welcher komplett bei der ThyssenKrupp Steel Europe AG hergestellt wurde.

8.8. Abstract

In order to improve the mechanical properties of dual phase steel, it is crucial to adjust the microstructure, consisting of martensite and ferrite, in an optimal way. To achieve this, both the applied heat treatment as well as the influence of the alloying elements has to be taken
into account. Regarding the alloying elements, not only the average concentration levels have to be considered, but the local concentration levels are of great importance, too.

The present thesis focuses on the influence of two different microstructures obtained after hot rolling on the properties of a completely processed dual phase steel. The first microstructure consists of a ferrite matrix with single carbides, martensite and bainite regions embedded in (B+M). The second one consists of a ferrite matrix with pearlite islands as well as single carbides embedded in (P+F). In order to analyse the distribution of the substitutional elements in both microstructures, they were examined by using extraction replicas and microprobe measurements. It was found that in the case of the P+F microstructure the single iron carbides as well as the iron carbides in pearlite were enriched with Mn and Cr. Additionally, some regions were depleted of Mn and Cr. In the case of the B+M microstructure it this was not the case.

After the characterisation of the hot rolled state of the material, both microstructures were annealed in a dilatometer. Here, the heat treatment was adjusted in a way which is comparable to the one used by Thyssenkrupp-Steel Europe to create a dual phase steel. During the applied heat treatment the material was reaustenized at 840 °C and cooled to room temperature afterwards. It was found that in the case of the P+F microstructure the reaustenization was not completed. This behaviour was contributed to the Mn depleted regions, which slowed down the transformation of bcc to fcc. In contrast to that, the B+M microstructure was completely reaustenized. Measuring of both microstructures during cooling down the start temperature of the growth of ferrite revealed that in the case of B+M ferrite formed at lower temperatures than in the case of P+F. In addition to that, the B+M microstructure had a higher martensite content. EBSD measurements which were performed after complete heat treatment revealed that the P+F dual phase steel had a lower average GND density in ferrite compared to the B+M dual phase steel. Thereby, the P+F dual phase steel showed ferrite regions which had GND density comparable to the average GND density of ferrite of B+M and ferrite regions which had a significantly lower GND density.

On the basis of further heat treatments, during which ferrite grew isothermally, the influence of the growth temperature of ferrite on its GND density was examined. It was proven that the average GND density of ferrite is inverse proportional to its growth temperature. An exceptional increase of the average GND density was found between 600 °C and 575 °C. This increase was much higher than the increase found between 650 °C and 600 °C or between 575 °C and 450 °C. Most likely a change in the growth mechanism of ferrite is responsible for the sudden increase of the average GND density. For 600 °C and higher temperatures a reconstructive growth mechanism is expected, for 575 °C and lower the growth mechanism
seems to have a more displacive character. However, the shape of the grains, which is often related to the growth mechanism of the grains, changes between 500 °C and 450 °C from globular to acicular. An acicular shape of the grains is known to be typical for bainite.

With the results of the last section it is possible to understand the inhomogeneous GND distribution found in the P+F dual phase steel after complete heat treatment. In the case of the P+F dual phase steel, ferrite grows at quite high temperatures (600 °C and higher) and lower temperatures. Since the GND density is inverse proportional to the growth temperature of ferrite, the GND density is distributed inhomogeneously in the ferrite. In the case of the B+M dual phase steel all ferrite growths at 510 °C, which leads to a more homogeneous distribution of high GND values.

The influence of the start distribution of Mn found in the hot rolled material was not only examined for the laboratory processed material but also for the material completely processed at ThyssenKrupp Steel Europe AG.
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