Nucleation of ferrite in austenite

The role of crystallography

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Background
1. Background

A long-standing problem in the field of materials science is the understanding of the grain nucleation mechanism in polycrystalline materials. The rate of grain nucleation has a strong influence on the overall kinetics of many phase transformations and recrystallization processes, which largely determine the final microstructure and thereby the mechanical properties of the material. Despite the worldwide scientific interest and technological relevance that has driven numerous studies on grain nucleation [1-4], the understanding of the underlying mechanisms is still limited. The understanding of grain nucleation is important for the steel industry for controlling the production process, the design of new steel grades with optimal mechanical properties, and the production of tailor-made steel.

In an early study, Clemm and Fisher have shown via calculations that for grain nucleation during solid-state phase transformations involving incoherent interfaces and grain boundaries, the effectiveness of the potential nucleation sites increases from homogenous nucleation, via nucleation on grain faces and edges to grain corners [1]. Due to the great experimental difficulties, there have only been few attempts to test this prediction experimentally. An exception is the work of Aaronson and co-workers, who measured ferrite nucleation rates on austenite grain faces in steel alloys with optical and electron microscopy techniques [2]. Their work shows that a nucleus with the shape of a pillbox and with coherent and semi-coherent interfaces matches better to their experimental findings than the Clemm and Fisher model involving a double spherical cap with incoherent interfaces [1, 2, 5]. The formation of a critical nucleus with the shape of a pillbox with (semi-) coherent interfaces at former austenite grain faces, leads to a lower activation energy for nucleation than the double-spherical-cap model, assuming typical interface energies for coherent and incoherent interfaces between ferrite and austenite in steel.

However, it was recently concluded from in-situ measurements with the three-dimensional X-ray diffraction microscope [6] that the activation energy for ferrite nucleation during the austenite decomposition in medium carbon steel is, unexpectedly, even smaller: two orders of magnitude smaller than predicted from the classical nucleation theory assuming a pillbox-shape for the critical nucleus and the interfacial energy values as determined by Lange III, Enomoto and Aaronson [2]. The nucleation mechanism that could explain this observation was not known, because the synchrotron measurements did not give information about the position at which the ferrite nuclei appeared in the austenite matrix and about the crystallographic orientation of the grains.

One possibility is that during the synchrotron measurements ferrite nuclei formed with mainly coherent interfaces between ferrite and austenite at former austenite grain corners. A study by Huang and Hillert [3] shows that grain corners are the most effective nucleation sites in the steel they studied. However, the nucleation mechanism is not entirely clear.

From the above studies it is clear that the type of potential nucleation site (corner, edge, or grain boundary face) and the crystallography of the grains (through the coherency of the interfaces involved) play an important role in grain nucleation during solid-state phase transformations. The exact character of this role, however, is far from clear.

1.1 Aim of the thesis

The scope of this thesis is to study the influence of crystallography on ferrite nucleation during the austenite to ferrite transformation in steel. The difference in crystallographic orientation between neighboring austenite grains, amongst other parameters such as grain boundary geometry, determines the $\gamma/\gamma$-grainboundary energy, and therefore the energy that is released during ferrite nucleation on that grain boundary. In addition, the formation of a new interface between the ferrite nucleus and the austenite grains requires energy. The energy of the austenite/ferrite interface is related to the crystallographic orientation and the shape of the boundary between the ferrite and (former) austenite grains.

The technique of Electron Backscatter Diffraction (EBSD) gives information about the type of nucleation site (grain boundary, edge, or corner) and about the crystallographic orientation. 3DXRD microscopy at synchrotron sources has been developed further and could also give information about the type of nucleation site and the crystallographic orientation. Both EBSD and 3DXRD microscopy are used in this thesis.

1.2 Contents of the thesis

The previously described aim of this thesis will be achieved step by step. In Chapter 2, solid-state nucleation is explained according to the classical nucleation theory and the experimental observations of several scientists in this field of Materials Science. Attention is given to the activation energy for nucleation that is directly influenced by the shape of the nucleus and the potential nucleation sites. The experimental observations include views on the potential nucleation sites, the nucleus shape and the influence of alloying elements on the activation energy for nucleation.
Chapter 3 concerns a description of the crystallographic orientation of the many grains in a metal and the interfaces that are formed between these grains. The methods of representing the crystallographic orientation are described, as well as the misorientation, i.e. the difference in crystallographic orientation, between two grains. Interfaces can have different structures and geometries, which influence the grain boundary energy. The specific orientation relationships between two different phases are described as well. The influence of these specific orientation relationships, the misorientation and the inclination angles on the interface energy is dealt with in the last section.

Chapter 4 introduces the diffraction techniques used for the experimental work in this thesis. First, the general theory of diffraction is described, followed by a description of the technique of Electron Backscatter Diffraction (EBSD) and the technique of three-dimensional X-ray diffraction microscopy. With these techniques information about the crystal structure and crystallographic orientation can be obtained either in two or three dimensions.

Chapter 5 investigates the role of grain and phase boundary misorientations during nucleation of ferrite in austenite. EBSD is performed on a high purity iron alloy with 20 wt.% Cr and 12 wt.% Ni with austenite and ferrite stable at room temperature in order to identify the crystallographic misorientation between austenite grains and between ferrite and austenite grains.

Chapter 6 investigates the role of crystallographic misorientations during nucleation of BCC grains on FCC grain boundary faces. Three-dimensional EBSD (3D-EBSD) is performed on a cobalt alloy with 15 wt.% Fe, which was heat-treated to have a microstructure with small BCC grains on FCC grain boundaries. 3D-EBSD allows to study the formation of multiple nuclei at the same grain boundary face. Variant selection during the formation of multiple nuclei at the same grain boundary face is investigated.

Chapter 7 describes 3DXRD-measurements that were performed at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France and the development of data-analysis strategies to determine the 3D microstructure of austenite without destroying the specimen. Measurements are performed on the same alloy as described in chapter 5, i.e. the Fe-20Cr-12Ni alloy.

1.3 References


Affiliation

The project is conducted at the Delft University of Technology as an in-kind contribution to the Materials Innovation Institute, M2i. Part of the research described in chapter 6 is conducted at the Ibaraki University in Japan as part of an internship under the supervision of Prof. M. Enomoto.
2

Solid-state Nucleation
Two main types of solid-state phase transformations can be distinguished in metals: diffusional and diffusionless phase transformations. The diffusionless transformation will not be considered in this chapter. An example of a diffusional transformation is the austenite-to-ferrite transformation in steel. Consider a carbon steel with a fully austenitic microstructure at a temperature above the A₃-temperature, i.e. the transformation temperature, see Figure 2-1, which is cooled slowly until below the A₁-temperature to become fully ferritic. In Figure 2-2, the possible evolution of the microstructure during different stages of the phase transformation of a fully austenitic structure to a fully ferritic microstructure is sketched [1, 2]. Nucleation most likely starts at grain corners and so called triple junctions, i.e. the location where three grain boundaries meet (see Figure 2-2b). In addition, nucleation will occur at grain boundary faces (see Figure 2-2c). These nuclei will grow into grains and will impinge (see Figure 2-2d). Furthermore, heterogeneous nucleation can occur at defects, like dislocations, within the austenite grains (see Figure 2-2e). These nuclei will grow into grains as well, until all of the austenite phase has transformed into the ferrite phase (see Figure 2-2f).

Figure 2-1: Partial Fe-C phase diagram.

Figure 2-2: Schematic illustration of possible phase transformation development:
a) austenite grain structure; b) ferrite nucleation on austenite grain corners; c) ferrite growth on grain corners and nucleation on grain boundary faces; d) ferrite growth on grain corners and boundaries and impingement on the grain boundaries; e) ferrite nucleation on defects in former austenite grain interiors; f) grain growth.
2.2 Classical Nucleation Theory

The classical nucleation theory has been summarized by Christian [3] and Kashchiev [4]. The classical nucleation theory gives an expression for the time-dependent nucleation rate (m⁻³ s⁻¹) for each type of nucleation site, J. In case several potential nucleation sites (grain corners, grain edges and grain faces, denoted by j) are activated in the system, the total nucleation rate is the sum of the nucleation rates of each site [5]:

$$J_{tot} = \sum_j J_j = \sum_j N_j \cdot \beta_j \cdot Z_j \cdot \exp \left[ -\frac{\Delta G^*}{k_B T} \right] \cdot \exp \left[ \frac{-\frac{\delta}{d_j}}{t} \right] = \sum_j J'_j \cdot \exp \left[ \frac{-\frac{\delta}{d_j}}{t} \right]$$

where $N$ is the density of potential nucleation sites (m⁻³); $\beta$ is the frequency factor, i.e. the rate at which single atoms are added to the critical nucleus (s⁻¹); $Z$ is the nonequilibrium Zeldovich factor, which takes into account the reduction in the equilibrium concentration of sub-critical nuclei due to the fact that some sub-critical nuclei become supercritical during the nucleation; $\Delta G^*$ is the activation energy barrier for nucleation; $t$ is the incubation time (s); $t$ is the isothermal transformation time (s); $k_B$ is the Boltzmann constant (1.38∙10⁻²³ J K⁻¹); $T$ is the absolute temperature at which the transformation takes place (K).

The density of the number of potential nucleation sites at grain faces, edges and corners, and in the interior of the parent grain depends on the grain size of the parent phase. Cahn [5] expressed the number of potential nucleation sites for each type of nucleation site per unit volume as:

$$N = n_v \left( \frac{\delta}{d} \right)^{v-3}$$

where $n_v$ is the number of atoms per unit volume, $\delta$ is an effective grain boundary thickness, $d$ is the diameter of the parent grain [5], and $v$ is the dimensionality of the nucleation site, according to Table 2-1. The number of potential grain boundary nucleation sites is therefore highest for homogeneous nucleation, followed by grain boundary faces, edges and finally corners.

### Table 2-1: Number of potential nucleation sites per unit volume, $N$, for different nucleation sites as a function of the austenite grain size $d_g$ and the effective grain boundary thickness $\delta$ or the critical dimension $\nu$.

<table>
<thead>
<tr>
<th>Nucleation Site</th>
<th>$\nu$</th>
<th>$N$ [3]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Homogeneous</td>
<td>3</td>
<td>$n_v$</td>
</tr>
<tr>
<td>Grain Boundary</td>
<td>2</td>
<td>$v_1 \left( \frac{\delta}{d} \right)$</td>
</tr>
<tr>
<td>Grain Edge</td>
<td>1</td>
<td>$n_1 \left( \frac{\delta}{d} \right)$</td>
</tr>
<tr>
<td>Grain Corner</td>
<td>0</td>
<td>$n_0 \left( \frac{\delta}{d} \right)$</td>
</tr>
</tbody>
</table>

**Activation energy for nucleation, $\Delta G^*$**

Upon cooling below the $A_s$-temperature, a thermodynamic driving force for nucleation of ferrite in the austenite matrix is generated. According to the phase diagram (Figure 2-1) the BCC structure becomes favorable below the $A_s$-temperature. During this decrease in temperature, small ‘clusters’ of atoms arrange into the BCC structure. Some clusters form a stable nucleus that is larger than a certain critical dimension and some clusters are not stable and disappear again.

One important assumption in the classical description of nucleation is that the interface between the nucleus and the matrix is sharp. Another important assumption is that the critical nucleus has a constant composition [6].

In the classical nucleation theory the Gibbs free energy change ($\Delta G$ in J) associated with the nucleation process is expressed as [1, 2]

$$\Delta G = -V (\Delta G_a - \Delta G_f) + \sum_i \Delta G_i$$

where $V$ is the volume of the nucleus (in m³); $\Delta G_a$ is the difference in Gibbs free energy per unit volume between the austenite ($G_a^*$) and ferrite ($G_f^*$); $\Delta G_i$ is also called the driving force for nucleation (in J m⁻³); $\Delta G_f$ is the misfit strain energy per unit volume that arises because the transformed volume does in general not fit perfectly into the
neglected, the critical dimensional parameter \( r^* \) becomes:

\[
r^* = \frac{2}{3} \sum z_i \sigma_{i} \frac{r}{(\Delta G - \Delta G})
\]

By substituting this value into Eq. 2-3, the energy value for the nucleation barrier (\( \Delta G^* \) in J) follows:

\[
\Delta G = \frac{4}{27} \left( \sum z_i \sigma_{i} \right)^2 \frac{r}{(\Delta G - \Delta G})^3
\]

The critical nucleus size, \( r^* \), is smaller when low-energy coherent interphases between the ferrite and austenite phases are created. A prerequisite for the formation of a coherent interface is that the nucleus has an orientation relationship with the parent grain [8]. Ferrite nucleation is therefore faster when the new nucleus has an orientation relationship with the surrounding austenite grains.

Since in homogeneous nucleation no former grain boundaries will be consumed, only the new boundary \( \sigma_{n} \) contributes to the critical Gibbs free energy (Eq. 2-5), which becomes

\[
\Delta G = \frac{16\pi}{(\Phi)} \frac{(\sigma_{n})^2}{(\Phi)} \frac{K_{\alpha}}{\Phi} = \Delta G - \Delta G
\]

in which \( K_{\alpha} \) is a geometrical dimensionless factor, introduced by Chan et al. [9] and is related to the shape of the critical nucleus, the type of nucleation site and the interfacial energies involved.

As outlined in the previous sections, all parameters appearing in Eq. 2-1, except \( k \), \( T \) and \( t \), depend on the type of nucleation site and/or the assumed shape of the critical nucleus (note that these two are not independent). Since the nucleation process is a statistical process and takes place in a small time span, it is very difficult to determine the specific site of nucleation. But it is almost impossible to determine the critical shape of the nucleus: when does a cluster disappear or when does it become a viable nucleus? The clusters that have disappeared cannot be identified in ex-situ experiments. In addition, the observed nuclei might have been growing considerably before detection and might have.
A Solute Rich Nucleus

For a solute rich nucleus it is required that the solute atoms move towards the nucleus. The frequency factor should be modified to take into account the concentration of the solute element:

$$\beta^* = \frac{6DS^*}{a} x_g$$  \hspace{1cm} 2-9

in which $x_g$ is the atom fraction of solute atoms in the matrix ($\gamma$).

A Solvent Rich Nucleus

A solvent rich nucleus requires movement of the solvent atoms to the critical nucleus. The frequency factor is now determined by the rate of addition of solvent atoms to the critical nucleus [12]. The disappearing of a single solute atom allows the addition of $(1-x_g/x_g)$ solvent atoms to the nucleus. Equation 2-9 should be multiplied by this factor. However, when the solute content is low ($x_g << 1$), like in low-alloyed steels, the equation can be simplified:

$$\beta^* = \frac{6DS^*}{a} x_g \cdot \frac{1-x_g}{x_g} \approx \frac{6DS^* (1-x_g)}{a} \approx \frac{6DS^*}{a}$$ (when $x_g << 1$)  \hspace{1cm} 2-10

The choice of the diffusion coefficient, $D$, in a two-component system is determined by the type of alloying elements [1]. Substitutional atoms usually diffuse by a vacancy mechanism, whereas the smaller interstitial atoms migrate by finding their way between the larger atoms, i.e. interstitially:

- For an interstitial element the diffusion coefficient of the rate-controlling element (solute or solvent) must be substituted in Eq. 2-9.
- For substitutional elements the number of vacancies present in the microstructure determines the definition of the diffusion coefficient equation.

The surface area of the critical nucleus $S^*$ is best described by being the interface of the nucleus on which new atoms can join the nucleus.

The derivation of the expression for the frequency factor, $\beta^*$, is complicated. As Russell [13] already stated, a proper choice of the frequency factor is not trivial. The frequency factor was first described using the classical transition state theory (Eq. 2-7), which is independent of the nucleus shape. But another description, given by Russell [11], takes into account the diffusion of atoms, the specific shape of the nucleus and the
For homogeneous spherical nucleation \( Z \) is

\[
Z = \frac{3}{4} \frac{V_z \sigma^2}{\sqrt{\pi k_b T \sum \sigma_i}}
\]

For homogeneous spherical nucleation \( Z \) is

\[
Z = \frac{\nu_r \sigma^2}{8 \pi \sqrt{k_b T} (\sigma_r)}
\]

The Incubation Time, \( \tau \)

The characteristic reaction time, also termed ‘incubation time’, follows from the frequency factor and the Zeldovich factor by:

\[
\tau = \frac{k}{2 \pi \nu^2 Z^2}
\]

where \( k \) is a dimensionless factor that varies from 0.5 to 5, depending on the particular derivation of \( \tau \) [11].

2.2.1 Activation energy for nucleation

The activation energy for nucleation is considered to be the most important factor in determining the nucleation rate. Equation 2-5 shows that the activation energy for nucleation depends on the driving force for nucleation, on the potential nucleation site, shape of the critical nucleus, and on the interface energies involved during nucleation. Each of these parameters is discussed in more detail in the sections below. The interface energy is considered separately in chapter 3 of this thesis.

Driving Force for Transformation, \( \Delta G \)

The driving force for nucleation is the difference in Gibbs free energy between the austenite matrix, \( G^* \), and the ferrite nucleus, \( G^' \), i.e. \( \Delta G^_n = G^' - G^* \). In Figure 2-4a the upper part of the low-carbon part of the phase diagram is enlarged and at the bottom the corresponding volume free energy curves of austenite and ferrite as a function of carbon content are displayed. On the left these curves are shown for temperature \( T_x \) and on the right for temperature \( T_y \) (with \( T_x > T_y \) as indicated in the phase diagram). Only the relative positions of the ferrite and austenite curves can be displayed, so a rise of the
nucleus composition $x_{C,\alpha}^e$ is removed from the austenite phase and the total free energy of the system decreases by an amount $\Delta G_1$, represented by point K in Figure 2-5. The ferrite nucleus is formed of this small volume of material that is rearranged into the ferrite BCC crystal structure. The total free energy of the system then increases by an amount $\Delta G_2$, represented by point L in Figure 2-5. The driving force for nucleation $\Delta G_n$ is simply the difference between $\Delta G_1$ and $\Delta G_2$, the length KL in Figure 2-5. The volume free energy change associated with nucleation is

$$\Delta G_n = \frac{\Delta G_n}{V}$$

where $V$ is the volume of the nucleus.

2.2.2 Shape of the nucleus and potential nucleation sites

Nucleation is facilitated on certain irregularities present in the parent phase. For instance nucleation on grain boundaries requires a lower $\Delta G^*$ than homogeneous nucleation for the same nucleus geometry and interface energies between the matrix and the nucleus. In this section nucleation on grain boundaries is considered. A distinction can be made between potential nucleation sites at grain faces (between two austenite grains), grain edges (between three austenite grains) and grain corners (between four austenite grains). The activation energy for nucleation strongly depends on the shape of the nucleus as
In this subsection the grain face nucleus model will be described. They only considered nucleation where no defects are present \((\Delta G_d = 0)\) and the misfit strain energy term \((\Delta G_m)\) is neglected. For the simple spherical caps models, in which the critical nucleus is part of a sphere with radius \(r\), and when the newly formed ferrite-austenite boundary energy is described by \(s_a\) and the disappearing austenite-austenite boundary energy by \(s_g\), the Gibbs free energy (compare Eq. 2-3) becomes:

\[
\Delta G = -z\sigma_a r^2 (\Delta G_d) + \sigma_a z_a^2 r^2 - \sigma_g z_g r^2
\]

in which the \(z\)'s determine the part of the sphere occupied by the nucleus. The value for the critical nucleus dimension \((r^*)\) is (compare Eq. 2-4):

\[
r^* = \frac{2(z_a^* - z_g^*)}{3} \frac{1}{z_a \Delta G_a}
\]

The energy value for the nucleation barrier becomes (compare Eq. 2-5)

\[
\Delta G^* = \frac{4}{27} \frac{(z_a^* - z_g^*)^3}{(z_a \Delta G_a)^2}
\]

The specific type of the spherical cap nuclei determines the values of the \(z\)'s and the equilibrium conditions for the interfacial areas determine the angle \(\Psi\), which is indicated in Figure 2-6. For the simple configuration of Figure 2-6a1 the static equilibrium condition is

\[
\sigma_a = 2\sigma_a \cos(\psi)
\]

and the geometrical parameters become:

\[
z_a^* = \frac{\pi \sin^3(\psi)}{3}
\]

\[
z_a^* = 4\pi (1 - \cos(\psi))
\]

\[
z_a^* = \frac{2\pi}{3} \left(2 - 3\cos(\psi) + \cos^3(\psi)\right)
\]

In Figure 2-6b some pillbox models are drawn, which were introduced in 1969 by Russell [11].

For the pillbox model of Figure 2-6b1 the shape factors are:

\[
z_a^{\text{pill}} = -\pi ; \quad z_a^{\text{pill}} = \pi ; \quad z_g^{\text{pill}} = \pi ; \quad z_a^{\text{pill}} = \frac{2\pi \cdot \varepsilon}{\sigma_a} ; \quad z_g = \frac{\pi \cdot \varepsilon}{\sigma_a}
\]

where
\[ e = \sigma_{\alpha}^i + \sigma_{\gamma}^b - \sigma_{\gamma}^s \] 2-25

and the \( \sigma \)'s are the interfacial energies as indicated in Figure 2-6b1. Substituting these shape factors in the nucleation rate equation (Eq. 2-1), the radius of the critical nucleus, \( r^* \), and the critical nucleus height, \( h^* \), become:

\[ r^* = \frac{-2\sigma_{\alpha}^*}{\Phi}, \quad h^* = \frac{-2e}{\Phi} \] 2-26

Incorporation of one or more incoherent (spherical) surfaces in the pillbox model (Figure 2-6b2 and Figure 2-6b3, respectively), leads to the following equations for \( \varepsilon' \):

\[ \varepsilon' = \sigma_{\alpha}^a + \sigma_{\gamma}^b - \sigma_{\gamma}^s = \sigma_{\alpha}^a + \sigma_{\gamma}^b \cos \psi - \sigma_{\gamma}^s \] 2-27

where all \( \sigma \)'s are indicated in the figures.

The main difference between the spherical cap models and the pillbox models is that the pillbox nuclei are thought to extend only into one parent austenite grain. An assumption is made for the derivation of the \( b^* \) term that atomic attachment is permitted only at the rim of the pillbox (at \( \sigma_{\gamma}^s \)). Curved interfaces are drawn to correspond to a disordered-type interface structure (incoherent with surrounding matrix) and a high interfacial energy, whereas faceted interfaces have a low interfacial energy and are (partly) coherent with the surrounding matrix. In Figure 2-6a2, a3 and a4 and b2 and b3 different variations with respect to the interfacial energies are shown. The general pillbox model of Figure 2-6b1 is assumed to be fully coherent will both austenite grains.

\[ z_1 = 3 \sin^2(\psi) \cdot \arccos \left( \frac{1}{2 \sin(\psi)} \right) - \cos(\psi) \cdot \sqrt{4 \sin^2(\psi) - 1} \] 2-28

\[ z_2 = 6 \pi - 12 \arcsin \left( \frac{1}{2 \sin(\psi)} \right) - 12 \cos(\psi) \cdot \arccos \left( \frac{\cot(\psi)}{\sqrt{3}} \right) \] 2-29

\[ z_3 = 2 \pi - 4 \arcsin \left( \frac{1}{2 \sin(\psi)} \right) + \frac{2}{3} \cos^2(\psi) \cdot \sqrt{4 \sin^2(\psi) - 1} + 2 \arccos \left( \frac{\cot(\psi)}{\sqrt{3}} \right) \cos(\psi) \cdot (3 - \cos^2(\psi)) \] 2-30

Figure 2-7: Clemm and Fishers [7] model for grain edge nucleation: a) three dimensional view of half the nucleus; b) cross-section of the critical nucleus.

Figure 2-8: Nucleus shape for a grain corners nucleated allotriomorph, according to Clemm and Fisher [7]: a) three dimensional grain shape; b) index of the four surrounding parent grains.

Nucleation on grain edges and corners

The equations derived by Clemm and Fisher for the shape factors (\( \varepsilon \)'s) (Eqs 2-21, 2-22 and 2-23) are different for nucleation of a nucleus composed of spherical caps at grain edges or grain corners. For a nucleus consisting of three spherical caps that formed at a grain edge, the shape factors \( z_1 \), \( z_2 \), and \( z_3 \) are:
For nucleation at grain corners, Clemm and Fisher assumed that the shape of the nucleus consists of four spherical caps as shown in Figure 2-8. The shape factors are even more complicated than for the edge-nucleated grains (Eqs 2-28 through 2-30). In analogy to the spherical cap models, the coherent nucleus on a grain edge is shown in Figure 2-9 and is referred to as an equilateral trigonal prism.

One of the main differences with the pillbox model for nucleation on grain faces is that this nucleus extends into three grains, while the grain face pillbox extends only in one parent grain. This corresponds well with experimental observations: the grain face nucleated grain is usually observed to extend into one parent grain, while the grain edge allotriomorph extends into three (or two) neighboring grains [22].

**Comparing nucleation sites**

To consider the differences between nucleation rates at different nucleation sites, the spherical cap models described by Clemm and Fisher [7] are used by Cahn [5] to discriminate between these sites according to nucleation characteristics. It is very likely that the different pillbox models for grain faces, edges and corners result in similar trends. From the spherical caps models (Figure 2-6a, Figure 2-7 and Figure 2-8) the values for the energy barrier, ΔG*, are calculated by Clemm and Fisher [7] and compared to the energy barrier for homogeneous nucleation (bulk nucleation, ΔG*_hom). In Figure 2-10 the calculated nucleation barriers are plotted against the interfacial energies (cos Ψ = σ_γγ/(2σ_αγ)). The main conclusion is that the energy barrier for nucleation on grain corners is smaller than for nucleation on grain edges, which in turn is smaller than for nucleation at grain faces for all combinations of interfacial energies.

When considering the number of these potential nucleation sites in a sample, it can easily be seen that the number of grain corners is lower than the number of grain edges, which in turn is lower than the number of grain faces. Nucleation might be fastest on
on grain corners; early site saturation will limit the nucleation rate at an early stage of transformation [5]. The two effects, the influence of the number of nucleation sites (Eq. 2-2) and the influence of the activation energy barrier, are compared by Cahn [5] by the introduction of the factor $R$:

$$R = \frac{\ln\left(\frac{d}{\delta}\right)}{-\Delta G_{\text{hom}}/k_BT} \tag{2-31}$$

In Figure 2-11 the values of $R$ (basically the influence of the initial austenite grain size) for particular interfacial energies ($\cos \Psi = \sigma /2\sigma_{ij}$) are plotted, together with their impact for the dominating type of nucleation sites. For a small initial austenite grain size (many grain corners) or a high $\Delta G_{\text{hom}}$ (determined by the values of the interfacial energies and the driving force), $R$ becomes low and the nucleation rate is dominated by grain corner nucleation for almost all interfacial energy values.

2.3 Experimental observations

In this subsection some experimental observations about nucleation are outlined. First a consideration about the nucleation sites is given, followed by a description of different nucleation sites and the influence of alloying elements on nucleation.

2.3.1 Nucleation sites

It follows from Eq. 2-3 that nucleation on defects reduces the change in Gibbs free energy for nucleation by $\Delta G_{\text{d}}$ and thereby facilitates nucleation of the new phase. Examples of defects are vacancies and dislocations. Homogeneous nucleation, i.e. nucleation in the grain interior of the parent grain, has the lowest nucleation rate. The presence of vacancies, dislocations, stacking faults and phase or grain boundaries all enhance the nucleation rate.

In an investigation by Enomoto et al. [22] nucleation rates at grain faces are compared to nucleation rates at grain edges. They conclude that at small undercoolings the grain edge nucleation is dominant over grain face nucleation and that at larger undercoolings of about 30-170°C, depending of the steel composition, the grain face nucleation is faster. The tendency of higher nucleation rates for grain edges at low undercoolings corresponds well with the predictions of Clemm and Fisher [7] described in the previous section.

Huang and Hillert [23] counted the number of nuclei on grain faces, on grain edges and on grain corners by careful sectioning (which results in an analysis in three dimensions) of a medium-carbon steel containing 0.51%C. Two stages in the transformation process are analyzed, the first stage at 0.05% ferrite, the second at 0.12% ferrite. By removing layers of about 5.3 $\mu$m, conclusions about the number of nucleation sites can be stated. Each allotriomorph is now identified either as face, edge or corner nucleated, i.e. the relative position of the ferrite nucleus compared to the austenite matrix is determined. In both specimens about 70% of the allotriomorphs was found to be nucleated on grain corners, followed by about 20-27% found on grain edges and only 4-7% on faces.

Huang and Hillert also conclude that the dominance of grain corners as nucleation sites is so strong that it may be suggested that the nucleation recorded as taking place at grain edges may actually have occurred at special points which are energetically similar to grain corners. In the samples used by Huang and Hillert annealing twins are commonly observed and therefore their intersections with grain edges might act as nucleation sites with similar nucleation characteristics as grain corners. Ignoring those observations leads to an even higher percentage grain corner nucleated grains.

Another observation made by Huang and Hillert is that the number of active nucleation sites is very low. Only about 5-7% of all grain corners actually contain ferrite nuclei, assuming that each austenite grain has on average 6-7 grain corners available for nucleation.

2.3.2 Nucleus Shape

Lange et al. [8] fitted experimental nucleation rates with the classical nucleation theory by considering different shapes and interface energies of the nucleus. The spherical cap models (see Figure 2-6a)) did not fit with any of the experimental observations at all. The pillbox shaped models, with one or more coherent interfaces fitted much better, but still did not predict the experimental observations completely.

To calculate the experimental nucleation rates, Lange et al. [8] considered three types of steel with different carbon contents. From optical microscopy, discrimination between the different nucleation sites, i.e. grain edges or faces, was made.

Since the austenite grain boundary faces are essentially perpendicular to the sample’s broad faces due to the small sample thickness of 100-250 $\mu$m, the probability of finding a ferrite crystal nucleated on a grain corner in the plane of polish is small enough to be disregarded. Differentiation between nucleation at grain faces and edges was made by considering the number of austenite grain boundaries in contact with the given ferrite
Counting of the allotriomorphs was established on a plane of polish, while one would like to know the three-dimensional nucleation characteristics. Schwartz and Saltykov [24-26] developed a method to determine the number of spherical particles per unit volume from measurements of the diameters of particles on a random plane of polish. This method can be applied using the following assumptions:

- All particles have a circular cross section in the plane of the grain boundary.
- The grain boundaries are perpendicular to the plane of polish.
- The largest diameter of the particles on the plane of polish is equal to the true diameter of the largest particle.
- The size distribution of circular sections in the grain boundary and the apparent diameters measured can be represented by a series of discrete size groups.

Under these assumptions, the Schwartz-Saltykov analysis is applied to the calculated number of ferrite allotriomorphs and gives the number of particles per unit unreacted area (instead of lines) of grain boundaries, $N_A$.

The last correction on the calculated nucleation rates is made by Woodhead [27] and DeHoff [28]. It is a correction for unresolved particles that is made by plotting the number of particles with a size $>R$ (the radius) as a function of $R$. Extrapolating to $R=0$ then gives the total number of particles per unit unreacted grain boundary area present at a given reaction time corrected for unresolved small particles. All correction methods applied by Lange et al. [8] increased the number of ferrite allotriomorphs per unreacted grain boundary area and also the nucleation rates for all samples.

Lange et al. [8] observed that there was only a small fraction of sites where nucleation took place, which was later also observed by Huang and Hillert [23]. Only one or two particles were seen on each grain boundary, but on most of the grain boundaries, about 2/3 of the total number of grain boundaries, there were no particles at all. Thus the allotriomorphs are very particular in the places where they originate. This may be influenced by the crystallographic orientation of the surrounding austenite grains, as explained in chapters 5 and 6 of this thesis. As described above, the experimentally measured nucleation rates are compared to the classical nucleation theory by considering different nucleus shapes indicated in Figure 2-6.

Although, the exact values of the interfacial energies (the $\sigma$'s in Figure 2-6) are not
equation to find the interfacial energy values (around 9 mJ/m²), from which the critical and experimentally determined rates differ by a factor of at least $10^{11}$.

Therefore the following approach is suggested: the pillbox model, as pictured in Figure 2-6b1, is assumed to represent the nucleus shape. The calculated steady state nucleation rate ($J_\text{s*}$) from experiments for the sample containing 0.13 wt% carbon and isothermally held at 825°C is 258 nuclei/cm² s, which was used as an input in the nucleation rate equation to find the interfacial energy values (around 9 mJ/m²), from which the critical dimensions of the pillbox were calculated (Eq. 2-26). These values are used to calculate the critical dimensions of the nucleus for all carbon contents. The calculated values for the critical nucleus height and diameter are a few ångströms (Å) and 20-30 Å, respectively.

The two modified pillbox models of Figure 2-6b2 and b3 give somewhat different values for the interfacial energies but within the same order of magnitude as for the general pillbox model. The correspondence of the experiments performed by Lange et al. [8] with the calculated nucleation rates with these three different pillbox models was quite good, but no discrimination between the three pillbox models could be made. However, King and Bell [29] observed orientation relationships between both austenite grains and the ferrite allotriomorphs, which means that the interfaces between the allotriomorph and the two neighboring grains forming the grain boundary on which the allotriomorph nucleated have low energy boundaries. Based on this observation, the fully coherent pillbox with interface boundaries having low energies (Figure 2-6b1) is thought to match best with the experimental observations.

The fully coherent pillbox model requires specific orientation relationships between the ferrite nucleus and both surrounding austenite grains. This requires an orientation relationship between the austenite grains, which are not likely to be abundantly present in steel [30]. Lange et al. [8] however conclude: Evidently there is sufficient texture in the austenite grains and enough symmetry associated with the FCC and BCC lattices so that (partially) coherent boundaries can be adequately approximated with the addition of supplementary networks of misfit dislocations and/or ledges over surprisingly wide ranges of orientations between the FCC and BCC lattices.

Measurement of nucleation rates is very difficult. The efforts of Aaronson and co-workers to determine the nucleation rates and their insight to replace the incoherent interfaces introduced by Clemm and Fisher [7] by (semi-)coherent ones, was quite revolutionary. However, some general remarks can be made on the experimental methods.

The experimenters [8, 18, 19] used very thin samples (100-250 µm) compared with the austenite grain size (ASTM 2-3; 120-160 µm) to eliminate grain corners from their calculations.

As the authors already stated, careful delineation of allotriomorphs on grain faces and edges is troublesome. The used tempering times and temperatures, 10 minutes at about 300°C, assisted in revealing the former austenite grain boundaries, but to what extend is not known.

The determination of the nucleation rates from the slope of the observed number of particles versus time is often based on only 2 or 3 data points. Determination of a slope between 2-3 measurements is not very accurate. The use of many different samples with locally different characteristics gives rise to a large scatter in the data points. Therefore the order of the ‘measured’ nucleation rates can be considered correct, but the actual nucleation rate value might differ from the given ones.

As Huang and Hillert [23] already mentioned, the real number of particles at short annealing times could be larger than according to observations, since some particles may be easily missed because of their small size. They state that it thus makes more sense to assume that all the particles form at an early stage of transformation, and to talk about the number of nuclei rather than about the rate of nucleation, which was used by Aaronson and co-workers.

All experiments are performed ex-situ, which could give different results than in-situ measurements because the starting parent microstructure is not the same for each sample. The former austenite grains have been transformed to martensite, so it is difficult to say something about the influence of the crystallographic orientation of the austenite grains on the measured nucleation rates, unless a reconstruction technique is used like the method developed by Decocker et al. [31]. In addition the influence of local inhomogeneities cannot be retraced.

Aaronson and co-workers compared their findings with the results of King and Bell [29], who, according to Aaronson and co-workers, found that the ferrite crystals had specific orientation relationships with both austenite grains that permitted the development of
closely aimed at the formation of pro-eutectoid ferrite from austenite at grain boundaries and therefore they did not take into account ferrite nucleation at grain edges and corners. They concluded that the ferrite nucleus has a specific orientation relationship with at least one austenite matrix grain on all the grain boundaries and that only at several boundaries the ferrite was allowed to have a specific orientation relationship with both austenite matrix grains, implying that the $\gamma/\gamma$ orientation relationships were not random in these cases [29].

Quantitative prediction of the (steady state) nucleation rate is quite difficult as the specific shape of the nucleus has a large influence on the calculated nucleation rate. In the nucleation rate equation, the activation barrier for nucleation appears in the exponent. Since the activation barrier depends on the difference in interfacial energies to the power of three, a large difference between the $\gamma/\gamma$-and the $\alpha/\gamma$-interfacial energy gives a large value in the exponent and subsequently dominates the overall nucleation rate. For the spherical caps model the grain boundary between the austenite matrix and the ferrite allotropic is assumed to be incoherent and thus has a high interfacial energy value. This makes the activation barrier (Eq. 2-5) high and the steady state nucleation rate drops immensely. The incorporation of coherent $\alpha/\gamma$ grain boundaries like in the pillbox model lowers the activation barrier and gives more realistic values for the steady state nucleation rate. However the exact shape of the nucleus is not determined yet. Another problem with the interfacial energies is that they are very hard to determine experimentally. The currently estimated values differ from about 10 mJ/m$^2$ for coherent interfaces to 600 mJ/m$^2$ for incoherent interfaces. In addition to this, the austenite microstructure might be inhomogeneous and subsequently the interfacial energies might also be inhomogeneous throughout the microstructure, which makes it difficult to quantify its values. Regions where the austenite grain boundary energy appears highest are probably among the sites where the ferrite nucleation appears first. Local inhomogeneities, for instance in chemical composition or temperature, have a great influence on the driving force for nucleation. A local pile up of any alloying element might alter the driving force for nucleation significantly.

The first introduced nucleus shapes [7] assumed incoherent interfaces of the nucleus with the matrix. However, experimental observations showed that the values of these interfacial energies were far too large to correspond with experimentally measured nucleation rates. The incorporation of coherent interfaces in the spherical caps models reduces the problem of the high interfacial energies, but it restricts the number of potential nucleation sites. For instance, for the coherent pillbox model (Figure 2-6b) the phase boundaries that are parallel to the parent grain boundary are assumed to have an orientation relationship with the surrounding parent grains. This already seems to exclude many potential nucleation sites for nucleation. As Kurdjumov and Sachs [32] derived in 1930, the orientation between an austenite matrix and the neighboring ferrite grains can be described by 24 variants of a specific orientation relation. When a nucleus has to be coherent with respect to two austenite grains, which also imposes an orientation relationship between the two austenite grains, the number of possible orientations of the ferrite grain is limited, and thus the number of potential nucleation sites is restricted. From the experimental observations the number of nucleation sites is indeed very low, and on a minor proportion of the grain boundaries (faces, edges or corners) nuclei are observed. Recent observations of grain rotation during annealing [33] suggest that during austenitizing atom-by-atom rotation of adjacent austenite grains towards energy cusp orientations occurs. This should markedly facilitate nucleation by pillbox-like critical nucleus shapes [20]. However, when considering the height of the nucleus, which is assumed to be only a few atoms high, it is hard to determine whether coherency or incoherency occurs.

Even when the critical nucleus height is more than a few atoms, it is difficult to understand how all ferrite nucleus interfaces could be coherent with the surrounding austenite grains. This becomes even more complicated for the ferrite grain that has nucleated on an austenite edge, shown in Figure 2-9. It should theoretically and mathematically be possible for a nucleus to be coherent with all three surrounding austenite grains, but the frequency of its actual occurrence in a microstructure is assumed to be very low. Therefore combinations of coherent, semi-coherent and incoherent interfaces for the critical nucleus shape on an edge seem to be appropriate.

The incorporation of coherent, semi-coherent and incoherent interfaces respectively diminishes one of the problems about the diffusion process. An incoherent interface (like the $\gamma/\gamma$ boundary) gives way to grain boundary diffusion, while a coherent interface restricts diffusion along the grain boundaries. With coherent interfaces the volume diffusion is thus dominating over the grain boundary diffusion.

From the experimentally measured steady state nucleation rates during the $\gamma$-$\alpha$ transformation in carbon steels, it can be concluded that when experimental steady state nucleation rates are compared with nucleation rates determined for the incoherent nucleus shape, they do not correspond at all. Incorporation of one or more coherent interfaces gives a better fit. Replacing incoherent interfaces with coherent interfaces lowers the interfacial energies from 600 mJ/m$^2$ to 10 mJ/m$^2$. The incorporation of coherent interfaces surrounding the nucleus corresponds to a nucleus having an
orientation relationship with the matrix.

2.3.3 Alloying Elements

In this section the influence of alloying elements in addition to carbon on the measured nucleation rates is analyzed. First the influence of one alloying element and later the influence of two alloying elements will be described.

One Alloying Element

Enomoto and Aaronson [18] investigated the influence of alloying elements on the measured nucleation rates in 1986. They considered five types of low carbon steels alloyed with either molybdenum (Mo), silicon (Si), cobalt (Co), nickel (Ni) or manganese (Mn). Again the procedures first described by Lange et al. [8] are applied to calculate the number of nuclei per unit area of unreacted austenite grain boundary. From the slopes of the \( N_f - t \) graphs the steady state nucleation rates are determined. However, in this paper the scatter in the \( N_f - t \) curves is used for the uncertainty in the nucleation rate: the upper and lower limit for the steady state nucleation rates are the maximum and minimum slopes drawn through the scatter bands. From these slopes errors of about 20-50% are deducted, with increasing errors at the lower temperatures, i.e. higher undercooling. Compared with the unalloyed sample containing 0.13wt% C errors of about 20-50% are deducted, with increasing errors at the lower temperatures, i.e. higher undercooling. Compared with the unalloyed sample containing 0.13wt% C investigated by Lange et al. [8], Enomoto and Aaronson [18] observed that Mn reduces the steady state nucleation rate most effectively, followed by Ni, Co, Mo and Si increase investigated by Lange et al. [8].

Errors of about 20-50% are deducted, with increasing errors at the lower temperatures, i.e. higher undercooling. Compared with the unalloyed sample containing 0.13wt% C investigated by Lange et al. [8], Enomoto and Aaronson [18] observed that Mn reduces the steady state nucleation rate most effectively, followed by Ni, Co, Mo and Si increase investigated by Lange et al. [8].

Table 2-2: Influence of alloying elements on the interface energy between austenite grains (\( \sigma_{ij} \)), the interfacial energy between the austenite and ferrite grains (\( \sigma_{Gv} \)), the driving force for nucleation (\( \Delta G \)), and the \( A_3 \)-temperature, which determine the steady state nucleation rate, compared to an unalloyed system. These data are valid at low undercoolings. Double arrows indicate a strong dependence.

<table>
<thead>
<tr>
<th>Alloying element</th>
<th>( \sigma_{ij} ) (mJ m(^{-2}))</th>
<th>( \sigma_{Gv} ) (mJ m(^{-2}))</th>
<th>( \Delta G ) (J cm(^{-3}))</th>
<th>( A_3 )-Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>( \downarrow \downarrow )</td>
<td>( \uparrow \uparrow )</td>
<td>( \uparrow \uparrow )</td>
<td>( \uparrow \uparrow )</td>
</tr>
<tr>
<td>Si</td>
<td>( \downarrow \downarrow )</td>
<td>( \uparrow \uparrow )</td>
<td>( \uparrow \uparrow )</td>
<td>( \uparrow \uparrow )</td>
</tr>
<tr>
<td>Co</td>
<td>( \downarrow \downarrow )</td>
<td>( \uparrow \downarrow )</td>
<td>( \uparrow \downarrow )</td>
<td>( \uparrow \downarrow )</td>
</tr>
<tr>
<td>Ni</td>
<td>( \downarrow \downarrow )</td>
<td>( \uparrow \downarrow )</td>
<td>( \uparrow \downarrow )</td>
<td>( \uparrow \downarrow )</td>
</tr>
<tr>
<td>Mn</td>
<td>( \downarrow \downarrow )</td>
<td>( \uparrow \downarrow )</td>
<td>( \uparrow \downarrow )</td>
<td>( \uparrow \downarrow )</td>
</tr>
<tr>
<td>0.13 wt.% C</td>
<td>715</td>
<td>180</td>
<td>-5.71</td>
<td>850</td>
</tr>
</tbody>
</table>

The observed characteristics of ferrite allotriomorph nucleation rates in the alloys studied are summarized as followed by Enomoto and Aaronson [18]:

- Mn and Ni reduce the nucleation rate of grain boundary ferrite allotriomorphs primarily by reducing the volume free energy change during nucleation at a given reaction temperature. Mn further reduces the nucleation rate presumably through diminishing the austenite grain boundary energy more than the austenite-ferrite phase boundary energy.
Si increases the nucleation rate because the negative volume free energy change accompanying the significant increase in the \( A_{\gamma} \)-temperature has a larger influence than the decrease of the nucleation rate due to the reduction of the austenite grain boundary energy.

Co has a weak effect on nucleation rates because it has only a minor influence on \( \alpha/\gamma \) phase boundary stability and a small tendency to segregate to austenite grain boundaries.

Mo increases the nucleation rates at high temperatures for the same reasons as Si. Extension of the measurements over a much wider temperature range shows a decrease in nucleation kinetics at lower temperatures.

An important factor to consider is that alloying elements change the temperature dependence of the driving force for nucleation, \( \Delta G_v \), and also the start temperature of the nucleation process, the \( A_{\gamma} \)-temperature. The alloying elements diffuse towards the grain boundaries thereby changing the interfacial energies and thus the energy barrier for nucleation. Mn, Ni and Si reduce the \( \alpha/\gamma \) interfacial energy more than they reduce the \( \gamma/\gamma \) grain boundary energy. Subsequently the nucleation barrier is increased and thus the nucleation rate is reduced by their influence on the interfacial energies.

Alloying elements influence the nucleation rates by segregating to the grain boundaries. Therefore, it is very well possible that the austenite grain boundary energies are anisotropic and that only particular sites support nucleation.

Two Alloying Elements

Tanaka et al. [19] measured grain face nucleation rates for steels containing 0.5 at% C with 3 at% Mn and 3 at% of a second alloying element X, being either Si, Ni or Co. Si was chosen because it is a ferrite stabilizer. Ni, on the other hand, is an austenite stabilizer and Co is regarded as approximately neutral with respect to such stabilization.

The experimentally observed nucleation rates were compared with the classical nucleation theory assuming a nucleus shape corresponding to the fully coherent pillbox. As mentioned for the Fe-C-X alloys, comparison between these nucleation rates is hard due to a different \( A_{\gamma} \)-temperature for each alloy and thus a different driving force at one particular (transformation) temperature.

The influence of the alloying elements on the volume free energy change was calculated using the central atoms model. This latter model was chosen because a previous study [34] had indicated that it can be more convenient for application to quaternary systems than for instance the Hillert-Staffanson model used for the one-alloying element systems before. From these calculations it is found that Si (the ferrite stabilizer) indeed increases the \( A_{\gamma} \)-temperature, while Ni (the austenite stabilizer) decreases it. Surprisingly, Co also raises the \( A_{\gamma} \)-temperature, while it should have been neutral in the stabilization process as this element is known as neither an austenite nor a ferrite stabilizer. Mn reduces the \( A_{\gamma} \)-temperature remarkably when compared with the Fe-C alloy, as is expected from an austenite stabilizer.

2.4 Acknowledgement

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2.5 References

3

Interfaces and crystallographic orientation
3. Interfaces and crystallographic orientation

3.1 Introduction

Clemm and Fisher [1] have theoretically shown that for grain nucleation during solid-state phase transformations the effectiveness of the potential nucleation sites increases from homogeneous nucleation, via nucleation on grain faces and edges to grain corners under the following assumptions: a) all interfaces between the nucleus and the matrix and between matrix grains are incoherent and b) the interface energies are isotropic.

Huang and Hillert [2] experimentally found that grain corners are the most effective nucleation sites in plain carbon steel. Lange et al. [3] studied ferrite nucleation on austenite grain faces in Fe-C alloys with optical and electron microscopy techniques. From their experimental work very low activation energy can be derived for ferrite nucleation. This activation energy is even lower than the energy required for grain corner nucleation according to Clemm and Fisher. In order to explain their experimental observations Lange et al. proposed that the shape of a critical nucleus is a pillbox with (partially) coherent interfaces that have low interface energy. The formation of coherent interfaces implies an orientation relation between the ferrite nucleus and neighboring austenite grains. This means that a limited number of parent grain boundary faces, i.e. grain boundary faces between two austenite grains having a specific orientation relation, are potential nucleation sites for nuclei with the geometry of a pillbox and coherent interfaces.

The interface energies involved in the nucleation process largely determine the activation energy for nucleation and thereby the nucleation rate. The role of both the geometry of the potential nucleation site and the crystallographic misorientations between the parent and product phase grains (through the coherency of the interfaces involved) in grain nucleation during solid-state phase transformations is reviewed in this chapter.

In section 3.2 the concept of microtexture is dealt with. Microtexture covers the field of crystallographic orientation at the grain level and the difference in crystallographic orientation between grains, called misorientation. This section covers some mathematics involved and the representation of microtexture. Section 3.3 deals with the geometry and energy of interfaces, in particular interfaces between grains of the same phase. However, the part on geometry is also applicable to interfaces between grains of different phases. Section 3.3.3 goes into more detail on the co-existence of two phases in a metal, especially austenite and ferrite in steel. It covers the orientation relationships between the two phases and the influence of the geometry and orientation of the parent phase (austenite or ferrite) grain boundary on the grain boundary energy, and indirectly on the nucleation of the product phase (ferrite or austenite).

3.2 Crystallographic orientation

Most crystalline materials, e.g. metals and ceramics, are polycrystalline, instead of mono- or bicrystalline. They are composed of a multitude of individual crystallites or ‘grains’. This section is mainly based on the references [4-10] and deals with the crystallographic orientation of misorientation.

3.2.1 Crystallographic orientation representation

Crystallographic orientation refers to how the crystallographic unit cell in a crystallite is positioned in three dimensions relative to a fixed reference, normally related to the sample dimensions. When there is no preferred orientation or texture and all possible orientations occur with equal frequency, the grains in the material are randomly distributed. In most materials there is a preference for certain orientations, caused by thermal stress gradients during solidification from the melt or by crystallization of an amorphous solid, followed by further thermo-mechanical processing. This occurrence is known as preferred orientation or texture.
Texture is important because many material properties are anisotropic with respect to the crystallographic structure, and therefore are texture-dependent. Examples of properties that depend on the average texture are the Young’s Modulus, strength, and toughness. When these properties are measured in different directions (e.g., rolling direction or the transverse direction), different values are found.

To describe the orientations of crystallites in a polycrystalline material, a coordinate system $K_c$ in the investigated sample needs to be defined. The selection of these fixed coordinates is arbitrary, but in the case of sheet or foil, the axes conventionally coincide with the rolling direction (RD or X), transverse direction (TD or Y) and normal direction (ND or Z), see Figure 3-1. For wire and fibers only one direction, the fiber axis, is evident. This is the first coordinate axis and the second is placed perpendicular to it. As a result the third is defined.

For each crystallite a second coordinate system $K_s$ which is fixed with respect to the crystal axes, is chosen. These axes can be arbitrarily chosen, but they must be all the same for each crystallite. As a rule the most appropriate for the crystal symmetry is chosen. For cubic crystal symmetry the cube edge directions [1 0 0], [0 1 0] and [0 0 1] are chosen.

The definition of the crystallographic orientation of a grain is the position of the crystal coordinate system with respect to the reference coordinate system [6] and it is described by the rotation matrix $g$ that transforms the sample-fixed coordinate system $K_s$ into the crystal-fixed coordinate system $K_c$, i.e. $K_c = g K_s$.

The fundamental way of expressing $g$ is the rotation matrix. The rotation matrix is a square matrix of nine numbers, which are obtained in the following way: The first row of the matrix is given by the cosines of the angles between the first crystal axis, [1 0 0], and each of the three sample axes, X, Y, Z, in turn. These three angles, $\alpha$, $\beta$, $\gamma$, are labeled in Figure 3-1. The second row is given by the cosines of the angles $\alpha$, $\beta$, $\gamma$, between [0 1 0] and X, Y, Z. Similarly the third row of the matrix consists of the cosines of the angles $\alpha$, $\beta$, $\gamma$, between [0 0 1] and X, Y, Z. The complete matrix is:

$$
g = \begin{bmatrix}
\cos \alpha & \cos \beta & \cos \gamma \\
\cos \beta & \cos \gamma & \cos \gamma \\
\cos \gamma & \cos \gamma & \cos \gamma 
\end{bmatrix}
$$

The rotation matrix $g$ is orthonormal, which means that the inverse of the matrix is equal to its transpose ($g'^{-1} = g'$). The length of both rows and columns of the matrix is 1. The matrix $g$ contains dependent variables, since a crystal orientation needs only three independent variables to specify it. In fact, the cross product of any two rows (or columns) gives the third and for any row or column the sum of the squares of the three elements is equal to one.

Due to crystal symmetry the choice of the crystal reference system $K_c$ is not unique and therefore different solutions of the orientation matrix exist, of which the number depends on the sample and crystal symmetry. In case of cubic crystal symmetry, there are 24 symmetry axes.

Table 3-1: Matrices $T_l$ representing the 24 symmetry variants for the cubic system.

<table>
<thead>
<tr>
<th>$T_l$</th>
<th>$T_l$</th>
<th>$T_l$</th>
<th>$T_l$</th>
<th>$T_l$</th>
</tr>
</thead>
</table>
| $\begin{bmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1 
\end{bmatrix}$ | $\begin{bmatrix}
0 & 0 & 1 \\
0 & 1 & 0 \\
1 & 0 & 0 
\end{bmatrix}$ | $\begin{bmatrix}
0 & 1 & 0 \\
0 & 0 & 1 \\
1 & 0 & 0 
\end{bmatrix}$ | $\begin{bmatrix}
0 & 1 & 0 \\
1 & 0 & 0 \\
0 & 0 & 1 
\end{bmatrix}$ | $\begin{bmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1 
\end{bmatrix}$ |

Accordingly, there are 24 solutions for the rotation matrix of a material with cubic symmetry. These can be obtained by using so-called transformation matrices, which only consists of 0’s and 1’s. Therefore, the elements of $g$ do not change, but the rows and columns of the matrix are permuted to new positions. The 24 transformation matrices for all cubic variants are given in Table 3-1. Multiplying the original rotation matrix $g$ by each transformation matrix $T_l$ generates the 24 symmetry-related solutions $g'$:

$$
g' = T_l g$$
The Euler angles refer to three rotations, which, when performed in the right order, transform $K_s$ into $K_c$. There are several ways for expressing the Euler angles, but in this thesis the Bunge notation will be used \[10\]. The rotations are:

1. Over an angle $\phi_1$ about ND transforming TD into TD' and RD into RD'.
2. Over an angle $\Phi$ about axis RD', which transforms ND into ND' and TD' into TD''.
3. Over an angle $\phi_2$ about ND', which transforms RD' into RD'' and TD'' into TD'''.

These three rotations are shown in Figure 3-2, where ND is Z, TD is Y and RD is X.

Analytically, the three rotations are expressed as:

$$
\begin{bmatrix}
\cos \phi_1 & \sin \phi_1 & 0 \\
-\sin \phi_1 & \cos \phi_1 & 0 \\
0 & 0 & 1
\end{bmatrix}
$$

3-3

Both the rotation matrix and the Miller indices over-determine the orientation, since only three variables are needed to specify an orientation. The most established way of expressing these three numbers is in terms of the Euler angles, which exist in a coordinate system known as the Euler space.

There are orientations which, when denoted in the ideal orientation notation, appear very similar, but are not the same. In the cubic system there are, for the most general case, four different orientations, which have the same Miller indices families,

$$(h k l)<u v w>\text{: (hkl)[uvw], (hk'l)[uvw], (hkl)[uvw], (hk'l)[uvw]}.$$

Both the rotation matrix and the Miller indices over-determine the orientation, since only three variables are needed to specify an orientation. The most established way of expressing these three numbers is in terms of the Euler angles, which exist in a coordinate system known as the Euler space.

The most common way to denote an orientation is through the Miller indices. In order to express a matrix $g$ in equation 3-1 in Miller indices, both the first column (the sample $X$-direction (RD) expressed in crystal coordinates) and the last column (the sample $Z$-direction (ND) expressed in crystal coordinates) of the rotation matrix are multiplied by an appropriate factor that brings them to integers. They are then divided by their lowest common denominator and written conventionally as $(h k l)[u v w]$, or $<u v w>$ if non-specific indices are used. The $(h k l)$ indices refer to the crystallographic plane that lies in the rolling plane (Z). The $<u v w>$ indices refer to the crystallographic direction that is parallel to the rolling direction (X). In practice, the direction cosines from the rotation matrix are ‘idealized’ to the nearest low-index integer Miller indices.

There are orientations which, when denoted in the ideal orientation notation, appear very similar, but are not the same. In the cubic system there are, for the most general case, four different orientations, which have the same Miller indices families, $(h k l)<u v w>$:

$$(h k l)[uvw],(h'k'l'[uvw],(hk'l)[uvw],(hkl)[uvw]}.$$

Both the rotation matrix and the Miller indices over-determine the orientation, since only three variables are needed to specify an orientation. The most established way of expressing these three numbers is in terms of the Euler angles, which exist in a coordinate system known as the Euler space.

Analytically, the three rotations are expressed as:

$$
\begin{bmatrix}
\cos \phi_1 & \sin \phi_1 & 0 \\
-\sin \phi_1 & \cos \phi_1 & 0 \\
0 & 0 & 1
\end{bmatrix}
$$

3-3

By multiplying these three matrices, an expression for the rotation matrix in equation 3-1 in Euler angles is obtained:

$$
\begin{bmatrix}
\cos \phi_1 & \sin \phi_1 & 0 \\
-\sin \phi_1 & \cos \phi_1 & 0 \\
0 & 0 & 1
\end{bmatrix}
$$

3-4

Figure 3-2: Diagram showing how rotation through the Euler angles, in order of 1, 2, 3, describes the relation between $K_s$ and $K_c$ \[6\].
The Euler angles are periodic with period $2\pi$, $g\{\phi_1+2\pi, \Phi+2\pi, \phi_2+2\pi\}=g\{\phi_1, \Phi, \phi_2\}$. There is also a mirror symmetry in the plane $F_p$, $g\{\phi_1+\pi, 2\pi-\Phi, \phi_2+\pi\}=g\{\phi_1, \Phi, \phi_2\}$, see Figure 3-3. In the most general case the Euler angles are defined in the range $0° < \phi_1, \phi_2 < 360°$ and $0° < \Phi < 180°$.

The orientation can be represented as a point in a three-dimensional coordinate system with the Euler angles as coordinates, called the Euler space. The maximum size of the Euler space is the same as the definition range of the Euler angles (see above), which is necessary for the description of triclinic crystal symmetry and no sample symmetry. As the symmetry of both systems increases, the angle-ranges within the Euler space decrease, see Table 3-2. In the cubic system there are 24 subspaces in Euler space, which can be reduced to 8 subspaces according to the three 4-fold and six 2-fold axes ($90°/1$ and $180°/1$ rotations, respectively). The reason why the $120°/11$ is not included in Table 3-2 is that the further reduced Euler space would obtain a rather complex shape, see Figure 3-4.

Another way of expressing the orientation is through an angle/axis pair. This means that the crystallographic matrix $K_c$ is rotated over a single angle, provided the rotation is performed about a specific axis, to be transformed into $K_s$. The three independent variables that define the orientation are one for the rotation angle $q$ and two for the rotation axis $UVW$, since $UVW$ is normalized such that $U^2 + V^2 + W^2 = 1$, so the third index is redundant. The relation between the angle/axis pair and the rotation matrix $g$ is as follows and is also used for representing the difference in orientation between two grains (see section 3.2.2):

$$\begin{align*}
\cos \theta &= (g_{11} + g_{22} + g_{33} - \frac{3}{2})/2 \\
U &= g_{23} - g_{32} \\
V &= g_{31} - g_{13} \\
W &= g_{12} - g_{21}
\end{align*}$$

Table 3-2: The size of the Euler space according to crystal structure and sample symmetry.

<table>
<thead>
<tr>
<th>Crystal structure</th>
<th>Crystal symmetry</th>
<th>Sample symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\phi_1$</td>
<td>$\phi_2$</td>
</tr>
<tr>
<td>Orthotropic$^1$</td>
<td>$90°$</td>
<td>$90°$</td>
</tr>
<tr>
<td>Monoclinic$^2$</td>
<td>$90°$</td>
<td>$90°$</td>
</tr>
<tr>
<td>Triclinic$^3$</td>
<td>$90°$</td>
<td>$120°$</td>
</tr>
</tbody>
</table>

# 120°/11 symmetry not included

1 An orthotropic sample has at least 2 orthogonal planes of symmetry.
2 A monoclinic sample has only 1 plane of symmetry.
3 A triclinic sample has no symmetry at all.
The advantages of the Rodrigues-Frank space are:

- The axis of rotation gives the direction of the R-vector. Thus, rotations about the same axis lie on a straight line, which passes through the origin.
- The angle of rotation gives the length of the R-vector. Hence small rotation angles cluster close to the origin.
- Orientations that include a common direction, i.e. a fibre texture, lie on a straight line, which in general does not pass through the origin.
- The edges of zones in RF-space are straight lines and the faces of zones are planar.

3.2.2 Misorientation

Misorientation is the name for the difference in crystallographic orientation between individual grains relative to a fixed reference, which often coincides with the principal axes of one of the grains concerned.

The lattices of two grains can be made to coincide by rotating one of them over a specific angle about a single axis. An example of such an angle/axis pair, as it is called, is shown in Figure 3-7. The axis is given as a vector $UVW$ and the angle $\theta$, which describes how much a grain has to rotate around the axis $UVW$ to completely coincide with its neighboring grain.

Specification of the misorientation between two crystallites without indicating the orientation of the boundary plane requires three parameters. The rotation matrix $f$ describes this misorientation, just as $g$ describes the crystallographic orientation, according to

$$
\begin{bmatrix}
a_{11} & a_{12} & a_{13} \\
a_{21} & a_{22} & a_{23} \\
a_{31} & a_{32} & a_{33}
\end{bmatrix}
$$

where the three columns of $a_i$ are direction cosines, the same as in equation 3-1, but here the cosines refer to the angles between the crystal axes of both grains. For cubic systems only three independent parameters are involved, as the rotation matrix $f$ is orthonormal.
The rotation angle θ is given by:

\[ 2 \cos \theta + 1 = a_{11} + a_{22} + a_{33}, \]

and the direction of the rotation axis UVW is given by:

\[ \left[ (a_{22} - a_{33}) \ (a_{33} - a_{11}) \ (a_{11} - a_{22}) \right] \]

In section 3.2.1 the Rodrigues-vector has been introduced. This orientation representation is often used for representing misorientation. In this case UVW is equal to \([r_1, r_2, r_3]\) (see equation 3-9) and the R-vector is calculated according to equation 3-7. When the misorientation between two grains with cubic crystal symmetry is represented, the fundamental zone reduces to 1/48th of the RF-space for cubic systems (see Figure 3-25c). This is the case for misorientations between the ferrite and austenite phases in steels.

The R-F space has some characteristic points related to the disorientation. In Figure 3-5, the origin of the fundamental zone is represented by the green spot. The yellow spot indicates the 45°/<1 0 0> misorientation. This vector has its endpoint on the edge of the fundamental zone because of the cubic symmetry. Any misorientation \(q/<100>\) with \(q\) larger than 45°, can also be described by \((90°-q)/<1 0 0>\) and this point will again be situated within the fundamental zone. The center point of the truncated corner (dark blue) represents a 60°/<1 1 1> misorientation. The point at the largest distance from the origin (pale blue) represents the largest possible misorientation for cubic crystals 62.8°/<1 1 0.414>, as shown in Figure 3-6.

Usually, grain boundaries are divided into two groups: high angle boundaries and low angle boundaries. The angle that separates these two groups is approximately 15°. Between 10° and 15° a transition takes place and it then becomes difficult to choose to which group the interface belongs to.

A low angle boundary can be represented by a series of dislocations. The simplest low angle boundary is the symmetrical tilt boundary, in which the lattices on both sides of the boundary are related by a misorientation about an axis in the plane of the boundary, see Figure 3-8a. A tilt boundary consists of a series of edge dislocations. The counterpart of a tilt boundary is a twist boundary, which consists of a series of screw dislocations and has a rotation axis perpendicular to the boundary plane, see Figure 3-8b.
3.3 Interfaces

The nature of any boundary depends on the misorientation of the two neighboring grains and the orientation of the boundary plane between the two grains, see Figure 3-10. A grain boundary is the boundary between two neighboring grains having the same crystal structure, but different crystal orientations. An interphase is a boundary between two neighboring grains of different crystallographic structure. Both are called interfaces; however, the former are homophase interfaces and the latter heterophase interfaces.

This section deals with the different geometries of interfaces in general in subsection 3.3.1 (based on references [4, 7, 12]) and with the grain boundary energy in particular in section 3.3.2 (based on references [7, 13, 14]).

### 3.3.1 The geometry and structure of interfaces

The structure of low angle boundaries is quite well understood, but much less is known about the structure of high angle boundaries. Early theories suggested that they consisted of a thin ‘amorphous layer’, but now it is known that these boundaries consist of regions of good and bad matching between the two grains. This theory is known as the concept of the coincidence site lattice (CSL).

When an atomic position deviates from the equilibrium position, the free energy will increase. From the preference for the lowest free energy it can be assumed that a crystal will try to keep its atoms in the ideal position as much as possible, even near a boundary. If orientation relationships exist some crystallographic planes continue from one crystal to the other, despite of the difference in orientation. These points are called coincidence sites. The orientation relationships can be described by a rotation of two planes relative to each other and in this way the coincidence conditions can be examined.

A coincidence plot is the most visual way to represent a CSL, at least in two dimensions. For other misorientations between adjoining grains a proportion of lattice sites will coincide, while forming a periodic sub-lattice in three dimensions. Then the parameter \( \Sigma \) is the volume ratio of the CSL unit cell, which is the group of atom positions that periodically coincide, to that of the crystal lattice.

In practice only CSLs having a relatively low \( \Sigma \) are of interest and these are shown in Table 3-3. Just as with the angle/axis pair it is enough to know only the lowest angle solution (the disorientation) to know which value \( \Sigma \) can be given to the CSL. The other solutions can be calculated using equations 3-1 and 3-2, and Table 3-1 given in section 3.2.1.

<table>
<thead>
<tr>
<th>( \Sigma )</th>
<th>( \theta )</th>
<th>( UVW )</th>
<th>( \Sigma )</th>
<th>( \theta )</th>
<th>( UVW )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>60</td>
<td>1 1 1</td>
<td>23</td>
<td>40.5</td>
<td>3 1 1</td>
</tr>
<tr>
<td>5</td>
<td>36.9</td>
<td>1 1 0</td>
<td>25a</td>
<td>16.3</td>
<td>1 0 0</td>
</tr>
<tr>
<td>7</td>
<td>38.2</td>
<td>1 1 1</td>
<td>25b</td>
<td>51.7</td>
<td>3 3 1</td>
</tr>
<tr>
<td>9</td>
<td>38.9</td>
<td>1 1 0</td>
<td>27a</td>
<td>31.6</td>
<td>3 1 0</td>
</tr>
<tr>
<td>11</td>
<td>50.5</td>
<td>1 1 0</td>
<td>27b</td>
<td>35.4</td>
<td>2 1 0</td>
</tr>
<tr>
<td>13a</td>
<td>22.6</td>
<td>1 0 0</td>
<td>29a</td>
<td>46.3</td>
<td>1 0 0</td>
</tr>
<tr>
<td>13b</td>
<td>27.8</td>
<td>1 1 1</td>
<td>29b</td>
<td>46.4</td>
<td>2 2 1</td>
</tr>
<tr>
<td>15</td>
<td>48.2</td>
<td>2 1 0</td>
<td>31a</td>
<td>17.9</td>
<td>1 1 1</td>
</tr>
<tr>
<td>17a</td>
<td>28.1</td>
<td>1 0 0</td>
<td>31b</td>
<td>52.2</td>
<td>2 1 1</td>
</tr>
<tr>
<td>17b</td>
<td>61.9</td>
<td>2 1 1</td>
<td>33a</td>
<td>20.1</td>
<td>1 1 0</td>
</tr>
<tr>
<td>19a</td>
<td>26.5</td>
<td>1 1 0</td>
<td>33b</td>
<td>33.6</td>
<td>3 1 1</td>
</tr>
<tr>
<td>19b</td>
<td>46.8</td>
<td>1 1 1</td>
<td>33c</td>
<td>59.0</td>
<td>1 1 0</td>
</tr>
<tr>
<td>21a</td>
<td>21.8</td>
<td>1 1 1</td>
<td>35a</td>
<td>34.0</td>
<td>2 1 1</td>
</tr>
<tr>
<td>21b</td>
<td>44.4</td>
<td>2 1 1</td>
<td>35b</td>
<td>43.2</td>
<td>3 3 1</td>
</tr>
</tbody>
</table>

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occur as well when the interfacial plane has a very different atomic arrangement in the two neighboring phases and a good matching is not possible across the interface. For a schematic overview of (in-)commensurate (semi-)coherent interfaces, see Figure 3-9.

3.3.2 Grain boundary energy

Grain boundaries have different properties than the lattice, because an excess of free volume and a lowered atomic coordination are the fundamental properties of a grain boundary. Since grain boundaries are basically defects, they have an energy associated with their non-equilibrium structure.

When the misorientation is small, the excess free volume is small and the atomic coordination is relatively high. This results in relatively low grain boundary energy. Small misorientations are mostly formed by a periodic dislocation distribution and are usually called small angle boundaries.

With the dislocation model, developed independently by Bragg, Burgers and several others, the grain boundary energy can be calculated for grains with small misorientation angles ($\theta \leq 15^\circ$), where the regions of atomic disorder do not overlap. The dislocation model is only valid when the dislocations are separated over a large number of atomic spacings, so that most of the lattices at the boundary are only elastically deformed.
The general equation for the grain boundary energy is [14]:

\[ E = E_0 [A - \ln \theta] \quad \text{(3-11)} \]

The parameter \( E_0 \) depends only on the elastic distortion and the grain boundary inclination angle \( \varphi \); it can be calculated from the dislocation model and the elastic constants of the material:

\[ E_0 = \frac{G\alpha(\cos \varphi + \sin \varphi)}{4\pi(1-\nu)} \quad \text{(3-12)} \]

where \( E_0 \) and \( A \) are independent of \( \theta \), \( G \) is the shear modulus, \( \nu \) the Poisson ratio and \( \alpha \) the lattice distance at the interface. The parameter \( A \) depends on the orientation of the grain boundary and the energy of the atoms at the dislocation itself, where some atoms do not have the correct number of nearest neighbors and the strain lies well out of the Hooke’s law range:

\[ A = A_0 - \frac{\sin 2\varphi}{2} - \frac{\sin \varphi \ln(\sin \varphi) + \cos \varphi \ln(\cos \varphi)}{\sin \varphi + \cos \varphi} \quad \text{(3-13)} \]

where

\[ A_0 = 1 + \ln\left(\frac{a}{2\rho_b}\right) \quad \text{(3-14)} \]

and \( \rho_b \) the radius of a small sphere around the dislocation, determined by the local energy of misfit, which must be calculated on an atomic basis.

In special cases, like the symmetrical tilt boundary (see section 3.2.2) \( \varphi = 0 \), the equation for the grain boundary energy can be simplified. If the spacing of the dislocations with Burgers vector \( \mathbf{b} \) in the boundary is \( D \), then the crystals on either side of the boundary have a misorientation of a small angle \( \theta \) :

\[ \theta = \frac{b}{D} \quad \text{(3-15)} \]

where \( b \) is the length of Burgers vector \( \mathbf{b} \). The energy of such a boundary \( E \) is given as in equation 3-11 where

\[ E_s = \frac{Gb}{4\pi(1-\nu)} \quad \text{(3-16)} \]

and

\[ A = 1 + \ln\left(\frac{b}{2\rho_b}\right) \quad \text{(3-17)} \]

For symmetrical tilt boundaries, \( \rho_b \) usually lies between \( b \) and \( 5b \). According to this equation, the energy of a tilt boundary increases with increasing misorientation (decreasing \( D \)) as shown in Figure 3-11. The combination of equations 3-11 and 3-15 shows that with increasing \( \theta \), the energy per dislocation decreases as shown in Figure 3-11, implying that a material will achieve a lower energy if the same number of dislocations is arranged in fewer, but higher-angle boundaries. However, when \( \theta \) exceeds 15°, the dislocation cores will overlap and equation 3-11 becomes invalid.

Sometimes it is convenient to use a normalized form of equation 3-11, where the energy \( E \) and the misorientation \( \theta \) are normalized to \( E_n \) and \( \theta_n \) when the boundary becomes a high angle boundary:

\[ E = E_n \frac{\theta}{\theta_n} \left(1 - \ln\left(\frac{\theta}{\theta_n}\right)\right) \quad \text{(3-18)} \]

where

\[ \theta_n = \exp(A - 1) \quad \text{(3-19)} \]

and

\[ E_n = E_0 \theta_n \quad \text{(3-20)} \]

representing the values of \( \theta \) and \( E \) when \( \theta \sim 15° \).

High angle boundaries are considerably more difficult to analyze, and the dislocation description no longer has a unique significance; the dislocations are so close together that their individual characters are lost. When \( \theta \) is so large that the dislocations are
perpendicular directions till its axial ratio is equal to unity, and through which the lattice change from tetragonal to cubic occurs. This mechanism has not been confirmed by experiments.

Kurdjumov and Sachs [19] found that in coarse-grained austenite, the Debeye circles in an X-ray diffraction pattern of the (011) planes of martensite or ferrite appeared mainly in the neighborhood of those of the (111) planes of austenite. From X-ray examination they found that the (011)- and (110)-circles obtained from martensite, coincided with the (111)-circle from austenite. They concluded that the {111} and {011} planes lie parallel to each other. As a result the [111] direction of martensite and the [101] direction of austenite are parallel to each other, see Figure 3-13. In Figure 3-13a the FCC unit cell is drawn with respect to the {111} plane and the BCC unit cell is drawn with respect to the {011} plane. Coincidently, these are the closed-packed planes of the crystal structures, respectively. From Figure 3-13b it can be easily observed how the re-arrangement of the atoms leads from a {111} base plane for FCC to a {011} base plane for BCC. Kurdjumov and Sachs agreed with Bain on the relative displacement among atoms while re-arranging from one crystal structure to the other, i.e. shear along (111), but not on the orientation relationship between the α- and γ-phase.

The Nishiyama-Wassermann relationship [20] is based on the X-ray examination of a single γ-crystal before and after transformation into a large number of α-crystals (no specification of martensite or ferrite) with the characteristic X-rays of molybdenum.

From the results and the comparison with the other two orientation relationships, Nishiyama concluded that the K-S and Bain orientation relationship are not exact, see

3.3.3 Orientation relations in steel

In general, orientation relationships are expressed in the following form [16]:

$\{hkl\} \{u,v,w\} \{u,v,w\}$

where subscripts 1 and 2 refer to the parent and the product phase, respectively.

In 'Worked examples in the geometry of crystals' by H.K.D.H. Bhadeshia [18] the mathematic relation between the orientation relations and the rotation matrix is given.

From the rotation matrix the Euler angles and the angle/axis pair can be calculated.

In many (alloyed) steels, austenite can transform into martensite (α‘), which has a body-centered tetragonal crystal structure, whereas ferrite (α) has the body-centered cubic crystal structure. During the investigation of the martensite formation in steel, several researchers found orientation relationships between austenite (γ) and martensite (α‘).

In total four different orientation relationships between γ (FCC) and α (BCC or BCT) have been found by Bain [17], Kurdjumov and Sachs [19], Nishiyama [20] and Wassermann [21], and Greninger and Troiano [22]. The last one is an intermediate between the Kurdjumov-Sachs and the Nishiyama-Wassermann relationships.

The orientation relationship of Bain is shown in Figure 3-12 [20]. The face-centered cubic lattice can be seen as a body-centered tetragonal lattice with an axial ratio of $\sqrt{2}$. According to Bain, the γ-to-α transformation is equivalent to a contraction in the direction of the long axis of the tetragonal lattice and a uniform expansion in the
Table 3-5: Lattice correspondences, minimal axis-angle pairs and Rodrigues-Frank coordinates for all Bain variants [38].

<table>
<thead>
<tr>
<th>Lattice correspondences</th>
<th>Minimum axis/angle pair</th>
<th>Rodrigues-Frank Coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100)γ // (100)α</td>
<td>45° (1 0 0)</td>
<td>(0.414 0 0)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(-0.414 0 0)</td>
</tr>
<tr>
<td>(010)γ // (010)α</td>
<td>45° (0 1 0)</td>
<td>(0 0.414 0)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0 0 -0.414)</td>
</tr>
</tbody>
</table>

The orientation relationships all have variants, according to the crystal orientations described in section 3.2.1. Because of symmetry, the number of variants is different for each orientation relationship. The differences are caused by the symmetry axes of the corresponding planes and directions. To obtain all variants, the orientation matrices of the orientation relationships are multiplied with the transformation matrices from Table 3-1.

However, these orientation relationships were found for the austenite to martensite transformation, which is a diffusionless transformation, whereas the austenite to ferrite transformation is a diffusional phase transformation. Brückner et al. [23] investigated whether the Bain, K-S or N-W orientation relationships would also hold for austenite and ferrite in ferritic low carbon steel. The K-S relationship dominated the orientation correlation of ferrite and austenite. Also some random orientation relationships were found, but there was no indication of a lattice correspondence according to Bain or N-W. In Table 3-4 the orientation relationships between austenite and ferrite that are known to exist, are listed, together with the corresponding crystallographic planes and directions, the general angle/axis pair representation and the number of variants for each orientation relationship.

In Table 3-5 to Table 3-7, the lattice correspondences of the crystallographic planes and directions, the minimum axis/angle pairs and the Rodrigues-Frank coordinates of the variants of the Bain, Kurdjumov-Sachs and the Nishiyama-Wassermann orientation relationships, respectively, are listed.
As mentioned before, the R-F vector of the angle/axis pair 45°<100> ends on the edge of the fundamental zone for cubic crystals in Rodrigues-Frank space, see Figure 3-5a. Therefore, this R-F vector has an equivalent point on the opposite face of the zone. This property of R-F vector is called degeneration of the minimum axis-angle representation.

In the axis/angle representation two different axes can be found for the same minimum angle of each lattice correspondence for the Bain orientation relationship (Table 3-5) and Nishiyama-Wasserman orientation relationship (Table 3-7). The original R-F vector is chosen as the R-F vector with the odd number of positive indices. The equivalent R-F vector has an odd number of negative indices and is put as second representation in Table 3-5 to Table 3-7.

The most common orientation relationships between FCC and BCC crystals vary from the K-S to the N-W orientation relationship. Usually a spread around these orientation relationships is taken into account. In between the K-S and N-W orientation relationship the Greninger-Troiano (G-T) orientation relationship can be found. In addition, an intermediate orientation relationship can be found in between the K-S and the Pitsch orientation relationships. This relationship is called the inverse Greninger-Troiano (G-T') orientation relationship. These specific orientation relationships are listed in Table 3-4 and are displayed in a [001] pole figure with the FCC parent crystal as a reference in Figure 3-15. It is observed that the K-S, N-W and Pitsch variants are symmetrically distributed around each Bain variant. Each K-S variant has an N-W variant and a Pitsch variant as a neighbor. In between a K-S variant and an N-W variant a G-T variant is found. In between a K-S variant and a Pitsch variant a G-T' variant is found. These variants form the so called Bain circles, showing the relationships between the specific orientation relationships [24].
Figure 3-15: The reflections of the variants of the specific orientation relationships from Table 3-4 on a [001] pole figure with the parent FCC crystal as a reference: A) All the reflections; B) Enlarged view of one of the Bain circles [24].

3.3.4 Interphase energy

For the calculation of interphase energies between $\alpha$ and $\gamma$ iron, Nagano and Enomoto [25] used the Embedded Atom Method (EAM). This model was developed by Daw and Baskes [26] for the modeling of impurities, surfaces and other defects in metals. Yang and Johnson [27] developed the EAM further, particularly for simulating the $\alpha$-$\gamma$ iron interface. The energy of the grain is calculated from the following equations:

$$E = \sum_i F(\rho_i) + \frac{1}{2} \sum_{i,j} \phi(R_{ij})$$

where $E$ is the total internal energy of the lattice, $F(\rho_i)$ is the energy required to embed atom $i$ into an environment with an electron density of $\rho_i$ (the embedding function), $\phi(R_{ij})$ is the two-body core to core potential between atoms $i$ and $j$ (two-body potential function) and $R_{ij}$ is the distance between atom $i$ and $j$. 

$$\overline{\rho_i} = \sum_{j \neq i} \rho_j(R_{ij})$$

where $\rho_j$ is the electron density at the location of atom $i$ due to all the other atoms in the lattice, $\rho_j(R_{ij})$ is the contribution from atom $j$ to the electron density at atom $i$ as a
function of the distance between the two atoms.

This EAM potential has the advantage that only one set of embedding and two-body potential functions is defined for BCC and FCC iron, thus it is not necessary to determine whether atoms belong to the BCC or the FCC lattice. Nevertheless, these functions are valid only for pure, unalloyed, iron and at the temperature of the two-phase equilibrium (912°C), as at this temperature the α-phase is not ferromagnetic (T_{Curie} = 770°C).

The third investigated orientation relationship was the cube-on-cube relationship, i.e. (100)_α//(100)_γ and [100]_α//[100]_γ, which may contain interphases with low coherency. The calculated energies are much higher than for the N-W and K-S related interphases.

![Figure 3-17](image1.png)

Figure 3-17: a) Variation of the interphase energy with inclination angle φ around the [001]_α//[−101]_γ-axis; b) 3D representation of an interphase rotated 13° around the [001]_α//[−101]_γ-axis from the closed packed planes, viewed in the direction parallel to the rotation axis [25].

The parameters in equations 3-22 and 3-23 were determined from the lattice constant of α and γ iron (0.2904 and 0.3647 nm, respectively), cohesive energy and the elastic constants of α iron, under the condition that the cohesive energies of the α and γ phases are the same at the equilibrium temperature. The α-γ interphase energies were calculated under the assumption of having a N-W, K-S or a cube-on-cube orientation relationship.

A schematic drawing of an interface between N-W related α and γ iron is shown in Figure 3-16. First, the interphase was rotated around the [001]_α//[−101]_γ-axis and the interphase energy was calculated at each interval of 10°, or smaller where necessary. From Figure 3-17a it can be seen that the interphase energy has a minimum at φ = 13°. In Figure 3-17b a 3D representation of an interphase inclined 13° around the [001]_α//[−101]_γ-axis is shown.

In Figure 3-19a, the variation of the interphase energy with inclination angle φ around the [−101]_α//[−121]_γ-axis is shown. In this case the interphase energy varied almost symmetrically with respect to φ = 90°.

The interphase plane of K-S related α-γ interphases were rotated around the [−111]_α//[−110]_γ-axis. The calculated interphase energies are plotted against φ in Figure 3-18a. The minimum energy was observed at φ = 160°, as shown in Figure 3-18b (arrow b), this interphase is parallel to (112)_γ.

The third investigated orientation relationship was the cube-on-cube relationship, i.e. (100)_α//(100)_γ and [100]_α//[100]_γ, which may contain interphases with low coherency. The calculated energies are much higher than for the N-W and K-S related interphases.

![Figure 3-18](image2.png)

Figure 3-18: a) Variation of the interphase energy with inclination angle φ around the [−111]_α//[−110]_γ-axis; b) 3D representation of an interphase rotated 16° around [−111]_α//[−110]_γ-axis from the closed packed planes, viewed in the direction parallel to the rotation axis [25].
The classical nucleation theory is described in Chapter 2 of this thesis. In this subsection, recommendations are done to implement microtexture into the nucleation model. For this purpose, some information from Chapter 2 will be repeated.

For the nucleation of ferrite (\(\alpha\)) in austenite (\(\gamma\)), a small volume with the \(\alpha\)-composition must be created and the atoms must rearrange in the BCC (\(\alpha\)) crystal structure. During the process an \(\alpha/\gamma\)-interface must be created, which leads to an activation barrier. The four contributions to the free energy change associated with nucleation are [7]:

1. At temperatures where \(\alpha\) is stable, the creation of a volume \(V\) of \(\alpha\) will cause a volume free energy reduction of \(V\Delta G_v\).
2. The creation of an interface with area \(A\) will give a free energy increase of \(A\sigma\).
3. Here we assume that the \(\alpha/\gamma\) - interphase energy is isotropic.
4. The transformed volume \(\alpha\) will not fit perfectly into the space of \(\gamma\), which gives rise to misfit strain energy \(\Delta G_s\) per unit volume of \(\alpha\).
5. If the creation of a nucleus results in the destruction of a defect, some free energy \((\Delta G_d)\) will be released, reducing the activation energy barrier.

These contributions lead to the following total free energy change:

\[
\Delta G = -V\Delta G_v + A\sigma + V\Delta G_s - \Delta G_d
\]

3-24

Because not all interfaces have the same misorientation, and therefore the same interface free energy, a more realistic representation of the total free energy change is reached when the \(A\sigma\) term is replaced by a summation over all surfaces of the nucleus \(\Sigma A\sigma\),

Especially the second term of equation 3-24, \(A\sigma\) is important for nucleation. \(A\sigma\) is a term that is determined by eight parameters that define \(\sigma\):

\[
\sigma = f(\theta, U, V, \Phi, \phi, T, P, C_i)
\]

3-25

where the angle \(\theta\) and \(U, V\) represent the boundary misorientation in angle/axis pair, \(\Phi\) represents the boundary inclination (the normal of the boundary plane), \(T\) is the temperature, \(P\) is the pressure and \(C_i\) is the concentration of impurities in the material and in general represents the chemical composition of the material.
Most of the time, $C_i$ is assumed to be zero, $T$ and $P$ are stated and $U$, $V$, $F_j$, $F_z$ are maintained constant and usually expressed in general notation like "UVW symmetrical tilt boundary." Equation 3-25 is then reduced to $\sigma = f(\theta)$ [29].

The interface free energy $\sigma$ can vary widely from very low values for coherent interphases to high values for incoherent interphases. The boundaries with the lowest energy are low-angle boundaries (small misorientation angles) and coherent twin boundaries. Of greater interest is the variation of energy with misorientation of medium- and high-angle boundaries which are not coherent twins [29].

![Figure 3-21: Representation of the 'Rotating ball' experiment [30].](image)

Chan and Balluffi [30, 33] and Gao et al. [34] did a number of experiments in which small single-crystal balls were sintered to large single-crystal plates at different misorientations, and interfaces, that run parallel to the plate, which were formed in the neck regions as illustrated in Figure 3-21 [15]. The misorientations were either of twist or tilt, depending upon whether the rotation axis was perpendicular or parallel to the interface. Upon annealing the balls spontaneously rotated around their tilt or twist axes in order to reduce the interface free energy. The interface inclination $\Phi$ remained parallel to the single-crystal plate and the only geometric variable, which changed was the crystal misorientation angle $\theta$. In a number of cases the rotating balls became trapped at specific rotation angles, indicating the presence of minima in the $\sigma = \sigma(\theta)$ function at these angles.

![Figure 3-22: Interface free energies $\sigma$ in aluminum for a) <100> twist boundaries and b) <110> tilt boundaries. Both curves show cusps at certain $\Sigma$-values [15, 31, 32].](image)

Otsuki and Mizuno [31, 32] examined the relationship between grain boundary energies and crystal orientations of boundary planes in aluminum. They made aluminum bi-crystals with <1 0 0> twist boundaries and <1 1 0> tilt boundaries. They reported a $s(\theta)$ curve for aluminum grains with <100> twist boundaries, which showed cusps at $\Sigma_{13A}$, $\Sigma_{17A}$ and $\Sigma_5$, see Figure 3-22a, and <110> tilt boundaries, which showed cusps at $\Sigma_3$ and $\Sigma_{11}$, see Figure 3-22b.

![Figure 3-23: a) Schematic representation of a SiO2 particle at a Cu-Cu grain boundary. b) Relative interface free energy against misorientation-angle diagram for [001] twist boundaries in copper at 1273K. The dotted line is for a random boundary [35].](image)

Mori et al. [35] calculated the relative interface free energy $\gamma / \gamma_i$ for SiO$_2$ particles in a Cu matrix, where $\gamma_i$ is the Cu/Cu interface free energy and $\gamma_i$ is the Cu-SiO$_2$ interphase free energy. The SiO$_2$-particles were spherical in the Cu-matrix, which indicates that $\gamma_i$ is isotropic. On a Cu/Cu interface, the SiO$_2$-particles become lenticular, which is a result of the Cu/Cu interface free energy $\gamma_i$. By measuring the longest and the shortest axis of the lense-shaped particle, the relative interface free energy $\gamma / \gamma_i$ can be calculated, see Figure 3-23.
From the information gained on the interface free energy $\sigma$ it is clear that the misorientation between neighboring grains is very important for nucleation of a new phase.

The interface free energy $\sigma$ is also dependent on the structure of the interface, especially whether the interfaces are grain faces (between two grains), grain edges (between three grains) or grain corners (between four grains). To show the influence of these interfaces on $\Delta G$, Figure 2-10 is reproduced, see Figure 3-25. However, this conclusion can be refined as the process the metal undergoes is very important as well. During deformation, dislocations are generated and will have a different distribution afterwards. Because of that nuclei can arise on other sites than grain corners, i.e. at locations with the most favorable misorientation between the adjacent (sub-)grains.

### 3.4 References


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4

Diffraction techniques for microstructural analysis
4. Diffraction techniques for microstructural analysis

4.1 Introduction

A complete characterization of the microstructure, i.e. the microscopic structure, of metals requires information about the position of each atom in the material over length scales of millimeters. This detailed characterization of microstructures is currently not possible. Three-dimensional atom probe (3DAP) has the ability to locate atoms in a relatively small volume of 10-20 x 10-20 x 50-60 nm³ [1, 2]. The drawback of 3DAP is that this is a destructive technique, since each atom is peeled off the material.

Historically, metallic microstructures were first characterized by light microscopy, which revealed the grain structure of metals and the morphology of the grains in 1887 by Sorby [3]. The distribution of the chemical elements could be measured at the level of micrometers later by means of Electron Probe Micro-Analysis (EPMA) in 1951 [4]. By 1981 it was possible to measure the distribution of crystal phases and the orientation of the crystals with EBSD. At that time it was already indicated that the resolution of EBSD could be less than 1μm [5].

Crystallographic texture data can be obtained by means of X-ray diffraction (XRD), neutron diffraction (ND), electron backscattering diffraction (EBSD), or selected area diffraction in a transmission electron microscope (TEM). In this work all experimental data were collected automated measuring techniques based on EBSD, and three-dimensional X-ray diffraction (3DXRD) microscopy using synchrotron radiation. The main advantage of these techniques is the possibility to gather local texture, i.e. the crystallographic orientation of individual grains, and microstructural information at the level of individual grains over lengths scales of millimeters. Standard laboratory XRD and ND measure the average texture in an area of several mm² and not at the level of individual grains. TEM covers the higher end of the resolution spectrum and has in some cases atomic resolution. However, a limited area (depending on the settings) can be investigated. For the present study TEM is not employed because of the limited sample volume that can be examined and the inherent poor data statistics.

The large majority of techniques for texture analysis are founded upon diffraction of radiation by a crystal lattice. So it is vital to understand this phenomenon in order to appreciate the principles upon which the various techniques for experimental texture measurements are based. In order to have diffraction of radiation at lattice planes, the wavelength of the incident radiation must be smaller than the lattice spacing. For the study of metals by means of X-ray diffraction the wavelength is typically tenths of a nanometer [6].

The general theory behind diffraction of radiation will be discussed in section 4.2. In section 4.3 the technique and theory of Electron Backscattering diffraction (EBSD) and OIM will be described and in section 4.4 three-dimensional X-ray diffraction (3DXRD) as developed at beamline 11, ID11, of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France, will be discussed.

4.2 The theory of diffraction

Electromagnetic radiation, e.g. light and X-rays, is diffracted by elastic scattering of the incident waves from the atoms of the sample material. Particle beams, e.g. beams of electrons, can also be considered as waves of radiation, with their wavelength given by the de Broglie relation:

\[ \lambda \propto \frac{h}{m} \]  

or

\[ \lambda = \frac{h}{\sqrt{2 \mu E_{\text{kin}}} \quad 4-1 } \]

where \( \lambda \) is the wavelength, \( h \) is Planck’s constant and \( m, v, E_{\text{kin}} \) are mass, velocity and kinetic energy of the particles, respectively. During scattering a plane (or spherical) wave of radiation interacts with an atom, which acts as a source of spherical waves of the same wavelength. In case radiation interacts with matter multiple atoms give rise to scattering and the scattered waves of individual atoms interfere to form a secondary wave. In most cases, the different waves will be out of phase, which leads to (partial) annihilation of the waves. The wave fronts will be in phase only at specific angles \( \theta \), meaning that at those angles diffraction of the incoming radiation can be observed. For this to occur, three conditions must be fulfilled:

- The atomic arrangement of the interacting material must be ordered, i.e. crystalline.
- The incoming radiation must be monochromatic, i.e. consisting only of one wavelength
- This wavelength must be of the same order of magnitude (or smaller) than the diffracting features.

The angle \( \theta \) at which diffraction occurs depends on both the wavelength \( \lambda \) and the spacing between the scattering atoms \( d \). Diffraction of radiation from the individual atoms in a crystal can be considered to be a reflection of radiation at a set of semi-
transparent mirrors, separated by a distance \(d\). Bragg showed that these mirrors are formed by atomic planes, i.e. the lattice planes \(\{hkl\}\), which are considered to be geometrically smooth.

Figure 4-1: Schematic drawing of Bragg’s law.

Figure 4-1 shows a lattice with three atom layers A, B and C with rays incident upon these planes in the direction LM at the angle \(\theta\). A small portion of the incident radiation will be reflected at an angle 2\(\theta\) at plane A, whereas the rest continues until it will be reflected at layers further down. The line L is drawn perpendicular to the incident beam to indicate the front of the approaching waves. In order to get a reinforced reflected beam in the direction MN, the waves must be in-phase along the line N. In order to achieve this, the path lengths for beams reflected at different consecutive layers in the crystal must differ by an integral number of wavelengths. In Figure 4-1 this means that the distance PM, P, i.e. the path difference between wave LMN and LM_{N}, is either one wavelength \(\lambda\) or a multiple \(n\lambda\). Usually only the first order diffraction \((n = 1)\) is considered. The other reflected beams have the same geometrical relationship, which is called Bragg’s law and is written as

\[
\lambda = 2d \sin \theta
\]

4-2

The specific angles at which diffraction is observed are called Bragg angles \(\theta_B\). Bragg’s law is an essential tool in texture research, because the orientation of a crystal can be identified from a measurement of the Bragg angles at which the waves of known wavelength are diffracted.

For most crystal structures, diffraction at the respective Bragg angles is not observed for all possible lattice planes. For body-centered cubic crystal structures (BCC) diffracting waves are extinguished when the sum of the Miller indices \(h + k + l\) is odd, i.e. diffraction occurs when \(h + k + l\) is even. For face-centered cubic (FCC) crystal structures diffraction is observed when the Miller indices \(h, k\) and \(l\) of the diffracting planes are either all odd or all even. In general, extinction occurs when there is an equivalent plane halfway between the planes that are in the Bragg position, i.e. extinction of BCC \(\{1 0 0\}\) planes through the \(\{2 0 0\}\) planes in between. The relative intensity of a given diffraction plane and, consequently, the rules of extinction, can be derived from calculation of the structure factor \(F\).

Diffraction of radiation at the different atoms in a crystalline structure is controlled by the structure factor, which is the unit cell equivalent of the atomic scattering factor \(f\). The efficiency of an atom in scattering radiation is usually described in terms of the atomic scattering factor. Since the intensity of a wave is the square of its amplitude, \(f^2\) is a measure of the intensity of the scattered wave dependent on the sort of atoms, scattering angle \(\theta\), the wavelength of the incident beam \(\lambda\) and on the kind of radiation.

Each atom \(j\) within a unit cell scatters radiation with amplitude proportional to \(f_j\) for that atom and with a phase difference with regard to the incident beam, determined by the position \((x_j, y_j, z_j)\) of that atom. Summation of the scattered waves gives the resultant wave reflected by the plane \(\{hkl\}\), which is called the structure factor:

\[
F = \sum_j f_j \exp[2\pi i(hx_j + ky_j + lx_j)]
\]

4-3

where \(i\) is the imaginary number \((i^2 = -1)\). The absolute value of the structure factor is the ratio between the amplitude of the wave scattered by all the atoms of a unit cell and the amplitude of the wave scattered by one electron. Since the intensity of a wave is proportional to the square of its amplitude, the intensity of the diffracted beam is proportional to \(F^2\) and diffraction only occurs if the reflected waves are all in phase, i.e. \(F \neq 0\).

For body-centered crystals, there are two atoms per unit cell, one at \((0, 0, 0)\) and the other at \((\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\). Putting these values in equation 4-3 the structure factor \(F\) becomes

\[
F = f \cdot \left[1 + \exp(2\pi i(h + k + l))\right]
\]

4-4

If \(h + k + l\) is odd, \(F\) becomes 0, but when \(h + k + l\) is even, \(F\) becomes \(2f\).

For face-centered crystals, a unit cell contains four atoms, which are positioned at \((0,0,0), (\frac{1}{2},\frac{1}{2},0), (\frac{1}{2},0,\frac{1}{2})\) and \((0,\frac{1}{2},\frac{1}{2})\). In this case the structure factor is

\[
F = f \cdot \left[1 + \exp(2\pi i(h + k)) + \exp(2\pi i(h + l)) + \exp(2\pi i(k + l))\right]
\]

4-5

If all three of \(\{hkl\}\) are either odd or even, the structure factor equals \(4f\) and diffraction
Figure 4-2: Summary of the various signals obtained from the interaction of electrons with matter in an electron microscope [6].

In a FEG-SEM (field emission gun SEM), see Figure 4-3, electrons are generated by the field emission (electron) gun using a high electrostatic field. Then the electrons are accelerated with an energy between 1 keV and 30 keV down the column towards the specimen. The magnetic lenses (condensor lens and objective lenses) focus the beam to a spot with a diameter of approximately 1-10 nm on the specimen. The electron beam is swept over the specimen surface by the scanning coils. The magnified image is formed by relating the detector signal to the position of the beam. The electrons used for conventional imaging are secondary electrons (see Figure 4-2) and are produced when loosely bound atomic electrons in solid matter are released by the interaction with the primary electrons. These secondary electrons have a small mean free path because
of their low energy. Therefore, the information in the image is obtained from a shallow depth (~ 10 nm).

In order to obtain an EBSD image, a stationary electron beam with an acceleration voltage of 20 to 30 kV strikes a tilted crystalline sample and the diffracted electrons form a so-called Kikuchi pattern on a fluorescent phosphor screen, as illustrated in Figure 4-4. This pattern is characteristic of the crystal structure and crystal orientation of the sample region from which it was generated. The EBSD sample is usually tilted at 70° to the horizontal to optimize both the contrast in the diffraction pattern and the fraction of electrons scattered from the sample. For smaller tilt angles the contrast in the diffraction pattern decreases. Due to the small spot size of the electron beam and the limited penetration depth of the backscattered electrons, the technique is very sensitive to imperfections of the sample surface and the sample preparation will therefore be of critical importance.

The formation of the Kikuchi pattern is based on the principle of diffraction. The electron beam collides with the sample, hereby causing the electrons to diverge in all directions from a point just below the sample surface and to impinge upon crystal planes in all directions. Two cones of diffracted electrons are produced, wherever the Bragg condition for diffraction is satisfied by a family of atomic lattice planes in the crystal. The fraction of the electrons that meet the Bragg condition for the encountered crystallographic plane will be diffracted into diffraction cones as shown in Figure 4-5. Due to the acceleration voltage of 30keV in the SEM, the de Broglie wavelength of the electrons is around 0.007 nm and the diffraction angle \( \theta \) is around 1.4°. The cones therefore intersect the phosphor screen as nearly straight lines and the bands can therefore be considered as a prolongation of the diffracting plane corresponding to the band. These cones are produced for each family of lattice planes and therefore a pattern of intersecting Kikuchi bands is observed on the phosphor screen as seen in Figure 4-4.

Only the electrons of the precise energy imposed by the Bragg condition contribute to the observed pattern. This fraction of electrons consists of elastically scattered electrons, the so called backscattered electrons. Inelastically scattered electrons, which have lost part of their energy, will produce a diffuse background in the pattern. The pattern is recorded by a sensitive (digital) CCD camera and the information is send to a PC where EBSD software automatically locates the positions of individual Kikuchi bands.

Since the Kikuchi bands can be considered as the prolongation of the diffracting planes on the phosphor screen, it is possible to determine the angle between two planes from their respective Kikuchi lines. This has been illustrated in Figure 4-6 which shows two Kikuchi lines, arising from different diffracting planes. Since all electrons are backscattered from the point (O) where the beam collides with the sample, the two diffracting planes are fully determined by the sets of non-collinear points (O, P, Q) and (O, R, S), respectively. The normal vectors \( n_1 \) and \( n_2 \) to these planes can be obtained as follows [9]:

\[
\vec{n}_1 = \frac{\vec{OP} \times \vec{OQ}}{||\vec{OP} \times \vec{OQ}||}, \quad \vec{n}_2 = \frac{\vec{OP} \times \vec{OS}}{||\vec{OP} \times \vec{OS}||}
\]

The angle between the crystallographic planes, involved can then be determined from the scalar product of the two normal vectors:

\[
\cos \gamma = \vec{n}_1 \cdot \vec{n}_2
\]
An orthonormal frame related to the Kikuchi pattern $e^p$ can be defined by employing the normal vectors of the crystal planes, constructed as follows:

\[
\begin{align*}
\mathbf{e}_1^p &= \mathbf{n}_1  \\
\mathbf{e}_2^p &= \mathbf{n}_2 \times \mathbf{n}_1  \\
\mathbf{e}_3^p &= \mathbf{e}_1^p \times \mathbf{e}_2^p
\end{align*}
\]

The resulting orthonormal basis is shown in Figure 4-7. The three unit vectors of the basis in the sample reference system $e^s$ are chosen along the rolling, transverse and normal direction, respectively. The basis related to the crystal reference system $e^c$ is formed by the three unit vectors along the crystal direction [100], [010] and [001].

The orientation of a crystal is, by definition, the description of the crystal axes in the sample reference system. This relation is deduced by considering three consecutive transformations. The crystal reference frame will be expressed in terms of the pattern reference frame, which will be expressed in terms of the screen reference frame, which in its turn will be expressed in terms of the sample reference frame. Combining these three transformations will eventually result in the transformation matrix, described in Chapter 3, between the crystal and sample reference system. Since the construction of the vectors, related to the basis $e^c$, is based on the known coordinates of points O, P, Q, R

The identification of the crystallographic planes, producing the observed bands, is based on the comparison of the measured angles with theoretical angles for the relevant phase which is a priori provided by the user, e.g. when measuring a cubic crystal structure, an angle of 54° indicates that the Kikuchi lines are arising from a {111}-plane and a {110}-plane. It is, however, not possible to determine which line arises from which plane when only two lines are available. Therefore, at least three Kikuchi lines are required to determine which line corresponds to which crystallographic plane.

In order to determine the crystallographic orientation, based on the observed Kikuchi pattern, the following four reference systems are introduced:

- a sample reference system (cf. chapter 3, section 3.1)
- a screen reference system (cf. Figure 4-7)
- a pattern reference system (cf. Figure 4-7)
- a crystal reference system (cf. chapter 3, section 3.1)
The transition from the crystal reference system to the sample reference system is made, using the intermediate pattern and screen bases:

\[
g_{ij} = g'_{ij} \cdot g''_{ij}
\]

As explained earlier, three sets of Kikuchi bands are required to characterize an orientation. If the captured Kikuchi pattern contains more bands than required (which generally is the case), the orientation is calculated repeatedly. The solution that is obtained most frequently is chosen as the orientation for the measured spot.

Orientation Imaging Microscopy® (OIM) is a commercial software package that automates the capturing and processing of the EBSD measuring system developed by TexSEM Laboratories Inc®. The idea is to scan the electron beam on a regular grid across a polycrystalline sample and measure the crystal orientation at each point. These crystallographic data points can be used to recompose an image of the microstructure which reveals the constituent grain morphology, orientations, and boundaries. A typical OIM-setup is presented in Figure 4-9.

The electron beam collides with the sample and a Kikuchi pattern is formed on the phosphor screen. This image is recorded by the CCD camera and is send to the computer which processes the pattern to determine the crystallographic orientation at the examined spot. Subsequently, the computer sends a signal to the hardware for the stage control which shifts the sample to the next spot of the area under investigation, following a hexagonal or rectangular grid, as shown in Figure 4-10. The step size is chosen by the

and S, the transformation matrix \( g' \) from pattern to screen coordinates can be calculated and is given by:

\[
g_{ij}' = e_i' \cdot e_j'
\]

The transformation from the sample reference system to the screen reference system can be deduced directly from the construction, presented in Figure 4-8.

\[
\hat{e}_i = -\hat{e}_2 \\
\hat{e}_2 = \hat{e}_1 \sin \alpha - \hat{e}_3 \cos \alpha \\
\hat{e}_3 = -(\hat{e}_1 \sin \alpha + \hat{e}_3 \cos \alpha)
\]

The transformation matrix \( g'' \) from screen to sample coordinates is calculated as follows:

\[
g_{ij}'' = -e_i' \cdot e_j'
\]

Finally the pattern reference system is expressed in terms of the crystal reference system. The first basis vector \( e_1^* \) is constructed as being the normal to the plane OQP in Figure 4-7. By employing the procedure as explained in equation 4-6, the Miller indices of the crystallographic plane involved can be determined. The unit vector \( e_1^* \) can therefore also be expressed in terms of the Miller indices:

\[
\hat{e}_1 = \frac{(hkl)}{[hkl]}
\]

A similar reasoning, concerning the construction of the vectors \( e_2^* \) and \( e_3^* \), leads to the following expressions:

\[
\hat{e}_2 = \frac{(hkl) \times (hkl)}{[hkl] \times [hkl]} \\
\hat{e}_3 = \hat{e}_2 \times \hat{e}_1
\]

Since these equations describe the pattern reference system in terms of the crystal reference system, the transformation matrix between the two respective bases can be determined:

\[
g_{ij}^* = e_i' \cdot e_j'
\]

The crystal-to-sample transformation matrix, i.e. the orientation matrix of the crystal, can now be calculated by combining the obtained transformation matrices \( g' \), \( g'' \) and \( g^* \).
user and is limited by the resolution of the SEM.

Using the post-processing software a wide variety of quantitative data can be obtained from the collected crystallographic information such as texture calculations (ODF, arbitrary pole figures and inverse pole figures and even pole figures outside the range of the XRD structure factor), grain size distributions, misorientation profiles, etc.

From the Kikuchi pattern, two additional parameters can be derived, namely the image quality (IQ) and the confidence index (CI). The image quality parameter quantifies the sharpness of the contrast of an electron backscatter diffraction pattern and can directly be related to the perfection of the crystal lattice in the examined region. This parameter depends on the material under investigation but is nearly independent of the crystal orientation. This allows several microstructural features to be distinguished on a map, using the image quality value as a gray scale legend, i.e. a light region indicates a high IQ while a dark region has a low IQ. The grain boundaries can be seen clearly on such a map since the lattice displays considerable lattice imperfections in the grain boundary area which results in a lower IQ. Another interesting feature that can be seen is the occurrence of a grayscale gradient within the grains which is due to a local higher dislocation density which disturbs the perfect lattice.

As mentioned before, each set of three Kikuchi bands in the observed pattern can be used to determine the crystallographic orientation. The orientation is determined for all possible sets \((N_{\text{tot}})\) and the most frequently occurring solution \((N_1)\) is chosen as the effective orientation. The confidence index \(CI\) is then defined as

\[
CI = \frac{(N_1 - N_2)}{N_{\text{tot}}} \tag{4-21}
\]

with \(N_2\) being the number of solutions resulting in the second most frequently obtained orientation. This parameter is often used as a threshold to determine which experimental points can be employed for further processing. As can be seen in Figure 4-11 the CI above 0.1 gives a correct indexed fraction close to 1. Therefore, a CI of 0.1 is usually the threshold value.

The CI is also an important parameter for the "clean-up" methods, provided within the OIM software. These algorithms allow altering the determined orientation and/or phase of single experimental points, based on correlation of its orientation/phase with those of the surrounding points. An example is given in Figure 4-12. The centre pixel does not belong to any grain; it has an orientation differing from all surrounding pixels. The clean-up procedure changes the orientation of the pixel to the orientation of the grain which has most neighboring pixels. If several surrounding grains would have an equal number of pixels adjacent to the one under consideration, one of them is picked at random. Once the dominant neighboring grain is determined, the orientation of the pixel is changed to match that of the neighboring pixel of the grain with the highest CI. Since the orientation of the experimental data is being changed, it is very important to avoid the introduction of artificial trends into the data. These algorithms show best results when the grain size is considerably greater than the step size of the scan.

![Figure 4-10: Hexagonal (above, red) or rectangular (below, blue) scan grid of the electron beam in OIM [10].](image1)

![Figure 4-11: Correct indexing as a function of the confidence index [9].](image2)

![Figure 4-12: Changing the measured orientation, based on correlation with the neighboring points [11].](image3)
Orientation contrast microscopy can also be used to identify the different phases present in a multiphase sample. The approach is to simply index the pattern according to the crystal structure parameter for each candidate phase. The indexing results are ranked according to a ranking factor based on the number of solutions and the confidence index or other parameters describing the indexing reliability. The phase with the highest ranking number is usually chosen as the identifying phase. A visual inspection of the indexing results can confirm that the computer correctly identifies the phases associated with each pattern.

4.4 Three-dimensional X-ray diffraction microscopy

4.4.1 Introduction

The traditional experimental techniques that have been available to study phase transformations, have limitations, which make it difficult to verify the nucleation theories described in chapter 2. Experimental techniques like dilatometry, differential scanning calorimetry and differential thermal analysis give in situ information about the overall transformation kinetics, but not on the nucleation and growth rates. Nucleation and growth rates can be determined from a series of cross-sections of quenched samples that are analyzed by optical and electron microscopy, but this is limited to ex-situ measurements. In-situ transmission electron microscopy studies are possible, but they are limited to the volumes of the thin lamellae and only give local information [12]. Altogether, the traditionally used experimental techniques cannot simultaneously provide in-situ information about grain nucleation and growth rates and the overall transformation rate. There is a need for experimental techniques that give more detailed information about the evolution of the microstructure during transformation and recrystallisation processes [13].

Recently, the development of X-ray microscopes and synchrotron sources with high energy X-rays created the opportunity to go one step further in the characterization of the evolution of the microstructure. The three-dimensional X-ray diffraction (3DXRD) microscope allows the in-situ study of individual grains in the bulk of a metal [15]. The 3DXRD microscope gives detailed information about the phase transformations in steel, which at present cannot be obtained with any other experimental technique. In particular, unique quantitative data is obtained about the nucleation rates and the growth rates of individual grains [16]. In addition, the 3DXRD technique gives information about the transformed fraction and the behavior of individual austenite grains.

X-rays interact with the electron cloud of the atom and therefore do not easily penetrate the bulk of a steel sample, as is the case for X-rays from conventional laboratory machines. However, hard X-rays (> 50 keV) from a synchrotron source have such high energies that it is possible to probe the bulk of steel. An X-ray beam of 80 keV penetrates through 4 mm of steel [17]. The in-situ synchrotron technique that was used for the research that is described in chapter 7 of this thesis is three-dimensional X-ray diffraction (3DXRD) microscopy.

3DXRD microscopy provides detailed information about polycrystalline materials. The power of the technique lies in the fact that it provides in-situ information about individual grains in the bulk of the material. Recent studies that used three-dimensional X-ray microscopy have led to new insight into grain rotation during deformation [18], the recrystallisation kinetics of grains during annealing [15], the austenite stability in TRIP steel during tensile testing [19], and the phase transformation kinetics in steel [14, 16, 20]. The experimental method and theory to study the phase transformation kinetics in steel with the 3DXRD microscope are treated in this section. A more detailed description and broader perspective of the use of the 3DXRD microscope can be found in the work of Poulsen and co-workers [21], who developed the 3DXRD microscope, and in particular the thesis of Lauridsen [20, 22].

4.4.2 Experimental method of three-dimensional X-ray diffraction microscopy

3DXRD microscopy can be performed only at synchrotron radiation sources because...
A high-intensity source is needed to obtain a sufficient signal-to-noise ratio. The first 3DXRD instrument was installed at the European Synchrotron Radiation Facility (ESRF) at the beamline ID 11. Figure 4-13 shows a schematic drawing of the experimental setup. To ensure a high penetration depth (e.g., 5 mm in steel and 4 cm in Al), the sample is illuminated by a monochromatic high-energy (50–100 keV) X-ray beam. A white synchrotron beam diffracts from a bent silicon Laue crystal or double Bragg crystals, which give a monochromatic (80 keV), vertically focused X-ray beam. Two sets of vertical and horizontal slits define the beam size, which was 400x1200 μm² in the case of the experiments described in Chapter 7. In this case, the beam was wider than the sample diameter.

In order to illuminate the sample uniformly, a homogeneous flux of photons is needed over the entire cross-section of the beam. The sample is positioned on a table, which can be translated in three directions (x, y, z) and rotated over an angle θ about an axis perpendicular to the incoming beam (see Figure 4-13). The diffracted X-rays are recorded with a 2D-detector. The sample is rotated in ω to probe the complete sample structure within the gauge volume and not just the parts that fulfill the Bragg condition.

Grains, cells, nuclei, and so on within the illuminated sample volume that fulfill the Bragg condition will generate a diffracted beam, which is recorded on a 2D detector [23]. Separate diffraction spots appear on the recorded diffraction pattern of which an example is shown in Figure 4-14. Each diffraction spot on the detector corresponds to a single grain in the material. The complete Bragg intensity of an individual grain is recorded by slightly rotating the sample about the z-axis (see Figure 4-13) over an angle Δω. The rotation angle Δω should be small enough to avoid overlap with reflections of other grains that are within the Δω-range of the measurement. It is not necessary that the rotation angle Δω is larger than the mosaicity of the grain as long as the complete Bragg intensity of a single grain is measured by taking multiple images by rotating over a number of Δω-steps. An optimum value of Δω needs to be found before the actual experiment is performed. In addition, the diffraction spots can overlap in the h-direction (see Figure 4-13) on the detector, but this can be controlled with the beam size.
to ferrite in-situ, where spatial information was not required.

In mode 2 the centre-of-mass position, volume, average orientation and average strain tensor can be determined for each grain in the illuminated part of the sample. The main difference between experiments in modes 1 or 2 is the $\omega$-range covered.

For modes 1 and 2 a far-field detector with a pixel size of $50 \times 50$ $\mu$m$^2$, such as a Frelon 2K or 4M detector, can be used. These far-field detectors can give very clear information on the crystallographic orientations in the sample [25].

Typical sample-detector distances range from 20 to 50 cm. In modes 1 and 2 hundreds of grains can be monitored simultaneously with a time resolution of the order of seconds, for grains as small as 20 nm [23].

![Figure 4-15: Schematic drawing of the experimental setup for the 3DXRD measurement, as in Figure 4-19, but now with a near-field detector, resulting in different diffraction patterns, i.e. the reflections have the shape of the reflected grains, instead of spots [23]. The Bragg angle $2\theta$, the rotation angle $\omega$ and the azimuth angle $\eta$ are indicated for the diffracted beam.](image)

With modes 3 and 4 a complete 3D map can be generated, including average crystal orientation, centre of mass position, volume and grain shape. In the case of an undeformed sample the orientation is, more or less, constant within each grain and a grain map can be provided (mode 3). In the case of a deformed sample, the orientation varies locally. For such a sample it is relevant to make an orientation map of every volume pixel (voxel) (mode 4). The main difference for experiments in modes 3 or 4 is the spatial resolution as for mode 4 every voxel has to be taken into account. For modes 3 and 4 a detector with a high spatial resolution is needed.

These detectors are near-field detectors, like a Quantix detector, with a spatial resolution of 3 to 10 $\mu$m, positioned close to the sample, e.g. 2 to 10 mm. Modes 3 and 4 have a low time resolution on the order of a few hours for a map of about 1,000 grains [24].

Separate diffraction spots appear on the recorded diffraction pattern of which an example is shown in Figure 4-19. The difference between the diffraction spots of Figures 4-14 and Figure 4-19 is that the spots on the near-field detector reflect the shape of the grains illuminated by the synchrotron beam. Thus the grain shape can be determined.

In all modes, in situ measurements can be performed using extra equipment like furnaces for heat-treatments and a tensile machine for in-situ tensile testing.

### 4.4.3 Theory of three-dimensional X-ray diffraction microscopy

The diffracted intensity per unit time of a single grain $I_g$, which is rotated through the Bragg-condition in order to illuminate the whole grain, can be written in the kinematic approximation as [26, 27]:

$$I_g = \Phi_\Omega \pi r_0^2 \frac{\lambda^2 F_{\Omega\Omega} V_g}{\Delta \omega \omega} P \exp(-2M), \quad 4.22$$

where $\Phi_\Omega$ is the incident flux of photons, $F_{\Omega\Omega}$ is the structure factor of the $\{hkl\}$-reflection, $\lambda$ is the photon wavelength, $V_g$ is the volume of the grain, $\Delta \omega$ is the angular range over which the grain is rotated, $\omega$ is the volume of the unit cell and $P$ is the polarization factor. The Lorentz factor of the grain is given by $L_g = 1/\sin(2q)$, where $2q$ is the scattering angle.

The Thomson scattering length $r_0$ is given by

$$r_0 = \frac{e^2}{4 \pi \varepsilon_0 m_c c} = 2.82 \times 10^{-15} \text{ m} \quad 4.23$$

where $e=1.602x10^{-19}$ C is the electron charge, $m_t = 9.1094x10^{-31}$ kg is the electron mass, $c = 2.9979x10^8$ m/s is the velocity of light, and $\varepsilon_0 = 8.85419x10^{-12}$ F/m is the permittivity of vacuum. The Debye-Waller factor $\exp(-2M)$ accounts for the thermal vibrations of the atoms, with

$$M = \frac{6h^4T}{mk_e \Theta^4} \left[ \left(\frac{x}{x\sin(\theta)}\right)^2 \right] \quad 4.24$$

where $h = 6.62608x10^{-34}$ Js is the Planck constant, $m$ is the mass of the vibrating atom ($m_{Fe} = 9.27x10^{-28}$ kg), $k_e = 1.381x10^{-23}$ J/K is the Boltzmann constant, $\Theta$ is the Debye temperature ($\Theta_{Fe} = 430$ K), $x = \Theta/T$ is the relative temperature, $T$ is the temperature, and

$$\phi(x) = \frac{1}{x} \frac{x}{\exp(x) - 1} d\xi \quad 4.25$$

where [28]
\[ \xi = \frac{h\nu}{\lambda kT} \]  

4-26

In the derivation of eq. 4-22 it is assumed that the single crystal rotates at a constant angular velocity about an axis perpendicular to the scattering vector and perpendicular to the primary beam. In this case a rotation \( \Delta \omega \) causes a change in the scattering angle of \( \Delta(2\theta) \). In the case that the scattering vector makes an angle \( \eta \) with the rotation axis (see Figure 4-13) unequal to 90°, the change in scattering angle is given by \( \Delta(2\theta) = \Delta\omega|\sin\eta| \). The total diffracted intensity of a single crystal can only be determined if \( \Delta\omega|\sin\eta| \) is larger than the mosaicity of the crystal. Note that the time that a grain is in reflection during rotation depends on \( \eta \). The diffracted intensity is independent of the rotation angle in the extreme case that \( \eta=0° \) (or 180°). The diffracted intensity from the \( \{hkl\} \)-planes of a single grain that makes an angle \( \eta \) with the axis of rotation can thus be written as

\[ I_\eta = \Phi \int \frac{\lambda^2 F_{\text{tot}}^2 V}{\Delta\omega|\sin\eta|\nu} L \exp(-2M) \]  

4-27

The integrated intensity \( I_\eta \) per unit time of a \( \{hkl\} \)-diffraction ring of a polycrystalline material, also named powder in diffraction terms, with random oriented grains is given by

\[ I_\eta = \Phi \int \frac{m_{\text{tot}} \lambda^2 F_{\text{tot}}^2 V(t)}{\nu} L \exp(-2M) \]  

4-28

where \( m_{\text{tot}} \) is the multiplicity factor of the \( \{hkl\} \)-ring and \( V \) is the volume of the diffracting phase. The Lorentz factor for a powder is given by \( L = 1/(4\sin(\theta)) \). The volume of the diffracting phase is given by

\[ V = f V \]  

4-29

where \( f \) is the volume fraction of the diffracting phase and \( V \) is the gauge volume, i.e. the measured volume, which is defined by the beam size and the thickness of the sample.

The volume of an individual grain is calculated from the measured grain intensity \( I_\eta \) normalized by the powder intensity \( I_\eta \) of the \( \{hkl\} \)-ring in which the reflection from the individual grain appeared. Combining equations 4-27 to 4-29 gives

\[ V = \frac{1}{2} m_{\text{tot}} \int \frac{\lambda^2 F_{\text{tot}}^2 V}{\nu} L \exp(-2M) \]  

4-30

However, the sample is being rotated over an angle \( \omega \), which gives different spots with a different intensity for every \( \Delta\omega \). To calculate the real intensity, we need to normalize the intensity by the rotation angle \( [29] \):

\[ I_\text{real} = \frac{I_\eta}{4\pi \sin^2(\theta)} \]  

4-31

In the case of a powder, the rotation over \( \omega \) gives the same intensity everywhere and the integrated intensity of the powder depends on the exposure time only and rotation of the powder does not have any effect:

\[ I_\omega = \Phi \int \frac{m_{\text{tot}} \lambda^2 F_{\text{tot}}^2 V}{\nu} L \exp(-2M) \]  

4-32

As explained above, the volume of an individual grain is calculated from the measured grain intensity \( I_\eta \) normalized by the powder intensity \( I_\omega \) of the \( \{hkl\} \)-ring in which the reflection from the individual grain appeared. Combining equations 4-31 and 4-32 with 4-29 gives

\[ V = \frac{I_\omega}{2L} \cos(\theta) \]  

4-33

When X-rays encounter any form of matter, they are partly transmitted and partly absorbed. Early on Röntgen established that the fractional decrease in the intensity \( I \) of the X-ray beam as it passes through any homogeneous substance is proportional to the transverse distance \( x \).

The following equation is used to calculate the absorption of X-rays:

\[ I = I_0 \exp(-\mu x) \]  

4-34

where \( I_0 \) is the intensity of the incident X-ray beam and \( I \) is the intensity of the transmitted beam after passing through a thickness \( x \).

The linear absorption coefficient \( \mu \) is proportional to the density \( \rho \), which means that the quantity \( \mu/\rho \) is a constant of the material and independent of its physical state (solid, liquid, or gas). This latter quantity, called the mass absorption coefficient, is the one usually tabulated. Equation 4-34 may be rewritten in a more general form:

\[ I = I_0 \exp(-\mu/\rho x) \]  

4-35

The amount of X-ray absorption when the beam is diffracted by the sample can be calculated using equation 7-1 with \( d = 1 \text{mm} \) being the diameter of the sample part penetrated by the beam, and \( 20 = 7.8444° \) being the diffraction angle of the \{200\}-lattice of the austenite phase at the surface of the sample, the distance travelled by the diffracted
The reciprocal lattice to a face-centered cubic (FCC) lattice is the body-centered cubic (BCC) lattice and the reciprocal lattice to a BCC lattice is the FCC lattice. The algebra for associating diffraction observations with reciprocal space is well described for single crystals. The polycrystalline case differs by the need for one extra coordinate system since the sample and the grains are separate objects. The single crystal formalism of Busing and Levy [30] is used, but a number of equations are put in alternative, equivalent expressions. In addition, the sign convention for \( \omega \) is opposite to the one used by Busing and Levy. An overview of the theory described hereafter can be found in [23].

Diffraction geometry

The reciprocal lattice plays a fundamental role in most analytic studies of periodic structures, particularly in the theory of diffraction. In crystallography, the reciprocal lattice of a Bravais lattice is the set of all vectors \( \mathbf{K} \) such that

\[
\exp(2\pi i \mathbf{K} \cdot \mathbf{R}) = 1
\]

for all lattice point position vectors \( \mathbf{R} \). This reciprocal lattice is itself a Bravais lattice.

For an infinite three-dimensional lattice, defined by its primitive vectors \( (\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3) \), its reciprocal lattice can be determined by generating its three reciprocal primitive vectors, through the formulas

\[
\mathbf{b}_1 = \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}
\]

\[
\mathbf{b}_2 = \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_2 \cdot (\mathbf{a}_3 \times \mathbf{a}_1)}
\]

\[
\mathbf{b}_3 = \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_3 \cdot (\mathbf{a}_1 \times \mathbf{a}_2)}
\]

Each point \((hkl)\) in the reciprocal lattice corresponds to a set of lattice planes \((hkl)\) in the real space lattice. The direction of the reciprocal lattice vector corresponds to the normal to the real space planes, and the magnitude of the reciprocal lattice vector is equal to the reciprocal of the interplanar spacing of the real space planes.

For Bragg reflections in neutron and X-ray diffraction, the momentum difference between incoming and diffracted X-rays of a crystal is a reciprocal lattice vector. The diffraction pattern of a crystal can be used to determine the reciprocal vectors of the lattice. Using this process, one can infer the atomic arrangement of a crystal.

The reciprocal lattice to a face-centered cubic (FCC) lattice is the body-centered cubic (BCC) lattice and the reciprocal lattice to a BCC lattice is the FCC lattice.

The algebra for associating diffraction observations with reciprocal space is well described for single crystals. The polycrystalline case differs by the need for one extra coordinate system since the sample and the grains are separate objects. The single crystal formalism of Busing and Levy [30] is used, but a number of equations are put in alternative, equivalent expressions. In addition, the sign convention for \( \omega \) is opposite to the one used by Busing and Levy. An overview of the theory described hereafter can be found in [23].

The laboratory and rotated coordinate systems

The laboratory coordinate system

Figure 4-16: Definition of the detector pixel coordinate system. The beam is directed perpendicular to the \((y, z)\) plane and towards the plane of the paper.

Each point \((hkl)\) in the reciprocal lattice corresponds to a set of lattice planes \((hkl)\) in the real space lattice. The direction of the reciprocal lattice vector corresponds to the normal to the real space planes, and the magnitude of the reciprocal lattice vector is equal to the reciprocal of the interplanar spacing of the real space planes.

For Bragg reflections in neutron and X-ray diffraction, the momentum difference between incoming and diffracted X-rays of a crystal is a reciprocal lattice vector. The diffraction pattern of a crystal can be used to determine the reciprocal vectors of the lattice. Using this process, one can infer the atomic arrangement of a crystal.

In this system the direction of the diffracted beam can be parameterized by the Bragg angle \( \theta \) and the azimuth angle \( \eta \), both defined in Figure 4-15. The angle \( \eta \) is defined as positive in the clockwise direction, when viewed from the sample towards the detector along the beam, and \( \eta=0 \) along the positive direction of \( \hat{z} \).

The rotation angle \( \omega \) is defined as positive in the counter clockwise direction parallel to \( \hat{z} \), viewed from the top. Then
• $\phi_x$: Tilt of detector around $x$;
• $\phi_y$: Tilt of detector around $y$;
• $\phi_z$: Tilt of detector around $z$;

All tilt angles are positive in counterclockwise direction around the rotation axes, i.e. right-hand system.

Correspondingly we have rotation matrices $R_X$, $R_Y$ and $R_Z$:

$$
\begin{pmatrix}
\cos(\phi) & -\sin(\phi) \\
\sin(\phi) & \cos(\phi)
\end{pmatrix}
$$

$$
\begin{pmatrix}
\cos(\phi) & 0 & \sin(\phi) \\
0 & 1 & 0 \\
-\sin(\phi) & 0 & \cos(\phi)
\end{pmatrix}
$$

Furthermore, the convention is that the detector system is rotated with respect to the laboratory system according to

$$R = R_X R_Y R_Z$$

The order of $R^x$, $R^y$ and $R^z$ is important even for relatively small tilts.

The detector has a pixel coordinate system and is a regular grid defined in pixels, as shown in Figure 4-16. Different detector systems use different conventions for how to flip the image and where to put the origin. The convention for the detector system at ID11 is defined below and used in the following equations.

The detector plane normal may be tilted with respect to the incoming beam. We define $(y_{raw}, z_{raw})$ to represent the corrected system:

$$(y_{raw}, z_{raw}) = SC(y_{raw}, z_{raw})$$

The detector plane normal may be tilted with respect to the incoming beam. We define

- $\phi_x$: Tilt of detector around $x$;
- $\phi_y$: Tilt of detector around $y$;
- $\phi_z$: Tilt of detector around $z$;

All tilt angles are positive in counterclockwise direction around the rotation axes, i.e. right-hand system.

Correspondingly we have rotation matrices $R^x$, $R^y$ and $R^z$:

$$
\begin{pmatrix}
1 & 0 & 0 \\
0 & \cos(\phi) & -\sin(\phi) \\
0 & \sin(\phi) & \cos(\phi)
\end{pmatrix}
$$

$$
\begin{pmatrix}
\cos(\phi) & 0 & \sin(\phi) \\
0 & 1 & 0 \\
-\sin(\phi) & 0 & \cos(\phi)
\end{pmatrix}
$$

$$
\begin{pmatrix}
\cos(\phi) & -\sin(\phi) & 0 \\
\sin(\phi) & \cos(\phi) & 0 \\
0 & 0 & 1
\end{pmatrix}
$$

Furthermore, the convention is that the detector system is rotated with respect to the laboratory system according to

$$R = R^x R^y R^z$$

The order of $R^x$, $R^y$ and $R^z$ is important even for relatively small tilts.

The relationship between a point on the detector as defined by pixel coordinates $(y_{det}, z_{det})$ and the corresponding point $(l_x, l_y, l_z)$ in the laboratory system is expressed by:

$$
\begin{pmatrix}
l_x \\
l_y \\
l_z
\end{pmatrix} = \Omega \begin{pmatrix} x_0 \\ y_0 \\ z_0 \end{pmatrix}
$$

By definition $(y_{det}(0), z_{det}(0))$ are the pixel coordinates for the reference beam, which is the incident ray passing through $(x_l, y_l, z_l) = (0,0,0)$, $P_x$ and $P_z$ are the pixel sizes in the directions $y$ and $z$ and $L$ is the distance from the centre of rotation to the point where the reference beam hits the detector.

**Diffraction**
Let \( u = G_l/\|G_l\|, \ y = G_s/\|G_s\| \) and \( h = \frac{BG_{w=0}}{\|B\|} \). Then

\[
\begin{pmatrix}
-\sin(\theta) \\
-\cos(\theta) \sin(\eta) \\
\cos(\theta) \cos(\eta)
\end{pmatrix}
\]

4-48

Forward projection

Let the diffraction take place at position \((x_l, y_l, z_l)\) in the sample system which is associated with a certain orientation \( U \). Assume further \( X \) and \( \Theta \), the spacegroup, the lattice parameters (and therefore \( B \)) and the x-ray wavelength are known. The task at hand is then to find the detector coordinates for the diffraction spot associated with a set of Miller indices \( G_{hkl} \). For each \( G_{hkl} \) firstly \( G_\omega \) is found. The \( \omega \)-position at which the diffraction condition is fulfilled is then given by

\[
\sin(\theta) = -u_1 = -[\Omega G_\omega]_1
\]

4-49

with \( \sin(\theta) \) defined by Braggs law. This is a quadratic equation for the determination of \( \omega \) given \( G_\omega \) and \( h \). The two possible solutions are

\[
\cos \omega = \pm \sqrt{\frac{a^2 + c^2 - b^2}{a^2 + b^2}}
\]

4-50

where

\[
a = G_{s,1} \frac{c}{|c|}, \quad b = G_{s,2} \frac{a}{|a|}, \quad c = \frac{\cos(2\theta) - 1}{\sqrt{2 - 2\cos(2\theta)}} \quad \text{and} \quad \sqrt{\delta} = a^2 + b^2 - c^2
\]

4-51

Depending on \( \omega \)-range none, one or two of these solutions may be real. Also note that eq. 4-50 has to be interpreted carefully to obtain \( \omega \), because the proper \( \omega \) fulfills both equations. Knowing \( \Omega G_l \) and \( u \) can be computed. In the case of an untilted detector:

\[
\begin{align*}
P_x(y_{s=0} - y_{w=0}) &= y_1 - (L - x) \tan(2\theta) \sin(\eta) \\
&= y_1 + \frac{(L - x) \tan(2\theta)}{\cos(\theta)} u_1 = y_1 + \frac{(L - x) \tan(2\theta)}{2 \pi \cos(\theta)} G_{s,2} \\
P_y(z_{s=0} - z_{w=0}) &= z_1 - (L - x) \tan(2\theta) \sin(\eta) \\
&= z_1 + \frac{(L - x) \tan(2\theta)}{\cos(\theta)} u_1 = z_1 + \frac{(L - x) \tan(2\theta)}{2 \pi \cos(\theta)} G_{s,1}
\end{align*}
\]

4-52

4-53
Grain indexing

A main task for 3DXRD programs is to index polycrystalline materials. Here a notation for the case of indexing a single crystal. It is assumed that the $B$ matrix is not known a priori.

For each spot on the detector we know $\Omega$, $X$, and $\Theta$, and as such $G_{\text{hkl}}$ can be determined. Associating these with a set of Miller indices $G_{\text{hkl}}$:

$$G_{\text{hkl}} = \Theta^{-1}X^{-1}\Omega^{-1}G_{\text{hkl}} = (UB)G_{\text{hkl}}$$  \hspace{1cm} (4-54)

The process of indexing is then the process of determining $(UB)$ or $(UB)^{-1}$ so that $G_{\text{hkl}}$ consists of simple integers. To continue the metric tensor $g^t = (UB)^{-1}(UB)$ is introduced:

$$g = \begin{bmatrix} a^2 & ab\cos(\gamma) & ac\cos(\beta) \\ ab\cos(\gamma) & b^2 & bc\cos(\alpha) \\ ac\cos(\beta) & bc\cos(\alpha) & c^2 \end{bmatrix}$$  \hspace{1cm} (4-55)

The unit cell volume is given by the determinant of $g$. Adding a "*" to all symbols the same relations in reciprocal space with $g^* = g^{-1}$ are obtained.

It turns out that (since $U = U^{-1}$):

$$g^* = (UB)^{-1}(UB) = BB^tB$$  \hspace{1cm} (4-56)

Knowing $g$ one can determine $U$ and $B$ by Cholesky [31] or QR decomposition. When the matrix $UB$ is nonsingular and the requirement is that the diagonal elements of $B$ are positive, see the definition of $B$ (equation 4-43), then the factorization is unique.

Representation of crystallographic orientation

Crystallographic orientations can be expressed in numerous ways, as described in detail in Chapter 3 of this thesis. For algebra the natural choice is the 3x3 orthogonal matrix $U$ or its inverse (and transpose) $g$, as defined above. For visualization and sampling a representation by three parameters is preferable. In the following definitions and summaries of the most important transforms and geometric properties for the representations in Euler angles and Rodrigues-Frank space are provided.

Euler angles (Bunge definition)

To represent the crystallographic orientation in Euler angles according to Bunge [32], the sample system $(e_1, e_2, e_3)$ is rotated around $e_3$ by $\phi_1$ first, subsequently around the new axis $e_1'$ by $\Phi$ and finally around the new axis $e_3''$ by $\phi_2$ to match the Cartesian grain system $(e_1'', e_2'', e_3'')$. The latter set is identical to the reciprocal axes ([100], [010], [001]) for cubic crystal systems. Traditionally, orientations are parameterized by a set of Euler angles $(\phi_1, \Phi, \phi_2)$, expressing subsequent rotations around three axes, as shown in Figure 4-17. With the definitions of the angles as provided by Bunge $U$ can be expressed as follows:

$$U = \begin{bmatrix} c(\phi_1)c(\phi_2) - s(\phi_1)s(\phi_2)c(\theta) & -c(\phi_1)s(\phi_2) - s(\phi_1)c(\phi_2) & s(\phi_1)s(\phi_2) \\ s(\phi_1)c(\phi_2) - c(\phi_1)s(\phi_2)c(\theta) & -s(\phi_1)s(\phi_2) + c(\phi_1)c(\phi_2) & c(\phi_1)s(\phi_2) \\ s(\phi_1)s(\phi_2) & c(\phi_1)s(\phi_2) & c(\phi_1) \end{bmatrix}$$  \hspace{1cm} (4-57)

$$U^t = \begin{bmatrix} c(\phi_1)c(\phi_2) - s(\phi_1)s(\phi_2)c(\theta) & -c(\phi_1)s(\phi_2) - s(\phi_1)c(\phi_2) & s(\phi_1)s(\phi_2) \\ s(\phi_1)c(\phi_2) - c(\phi_1)s(\phi_2)c(\theta) & -s(\phi_1)s(\phi_2) + c(\phi_1)c(\phi_2) & c(\phi_1)s(\phi_2) \\ s(\phi_1)s(\phi_2) & c(\phi_1)s(\phi_2) & c(\phi_1) \end{bmatrix}$$  \hspace{1cm} (4-58)

where $c$ and $s$ are short for cosine and sine, respectively. The reverse relationship is given by:

$$\phi_1 = -\arctan(U_{11}, U_{12})$$
$$\phi_2 = \arccos(U_{33})$$
$$\phi_3 = -\arctan(U_{12}, U_{11})$$

Note that the two-argument inverse tangent $\arctan(x,y)$ computes $\arctan(x/y)$, but results in the correct angle by taking into account in which quadrant $(x,y)$ lies. Calculating the combined rotation of two individual rotations is very cumbersome in the Euler angle representation. Therefore, for these calculations, i.e. calculating the misorientation, the orientation matrices $U$ or $g (=U^{-1})$ or the Rodrigues-Frank space are usually used.

Euler space is non-linear with singularities at $\phi = 0$ and $\pi$. In order to restore uniformity the use of the metric $dg$ is required [32]:

$$dg(\phi, \phi_1, \phi_2) = \frac{1}{8\pi^2} \sin(\phi) d\phi d\phi_1 d\phi_2$$  \hspace{1cm} (4-59)
In accordance with usual practice, the sign for summation over vector and tensor suffixes is omitted. Summation is understood with respect to all suffixes that appear twice in a given term according to the Einstein convention. The reverse relationship (determining $R$ given $U$) is defined by:

$$
R = \frac{\varepsilon_{jk} S_{jk}}{1 + g_{mm}}
$$

4-63

where $g_{mm}$ is the trace of $g$. The result $r_1$ of two rotations, first $r_1$ and then $r_2$ is

$$
R = R_2 R_1 - R_2 R_1 R_2
$$

4-64

The metric $d_{ij}$ and the volume element $dV$ are defined by

$$
d_{ij} = \frac{1}{(1 + R^2)} [ (1 + R^2) \delta_{ij} - 2 R_{ij} ]
$$

4-65

$$
dV = \sqrt{\text{det}(d_{ij})} = \frac{\sqrt{\text{det}(d_{ij})}}{1 + R^2}
$$

4-66

Evidently this leads to complications for $r \rightarrow \infty$ (that is for low crystal symmetry; see Chapter 3 of this thesis). On the other hand, for $\varphi \rightarrow 0$ rotations become commutative. This is reflected in the fact that the metric becomes linear. As an example, for orientation distributions characterized by $\varphi < 10^\circ$, the space is Euclidean within an accuracy of better than 1%.

4.4.5 Partial 3D-information by 3DXRD microscopy

As described in section 4.4.2, four distinct modes of 3DXRD microscopy are possible. The 3DXRD experiments performed and described in this thesis are all done in mode 2.
It is called partial 3D as the shape of the grains in the sample cannot be determined from the diffraction rings observed with the far-field detector. What can be determined are the centre of mass, volume and average orientation of the grains in the sample. With this information and a three-dimensional Voronoi construction it is possible to 'reconstruct' the microstructure.

In this mode of 3DXRD microscopy, the experiment is done three times, with the far-field detector at a different distance from the sample, as shown in Figure 4-19. In every experiment, the beam is diffracted by the grains in the sample over an o-range that is the same for every experiment. In this way all grains are diffracted three times and the spots will appear at the same locations in the diffraction rings. It is now possible to determine the centre of mass with ray-tracing.

4.5 References

10. R. Decock, Modelling the crystallography of the transformation of austenite to low temperature phases in Fe-based alloys, UGent, 2006

25. S. S. West, Nucleation of Recrystallization studied by EBSP and 3DXRD, Technical University of Denmark, 2009


The roles of crystal misorientations during solid-state nucleation of ferrite in austenite
5. The roles of crystal misorientations during solid-state nucleation of ferrite in austenite


5.1 Introduction

Understanding the grain nucleation mechanism during solid-state phase transformations in polycrystalline materials is an enduring problem in the field of materials science. The nucleation stage has a strong influence on the overall evolution of phase transformations and recrystallisation processes. This determines the final microstructure and thereby the properties of the material. The understanding of grain nucleation is important for controlling the production process, the design of new alloys with optimal properties, and the production of tailor-made alloys.

The experimental difficulty in the study of solid-state nucleation is caused by the fact that critical nuclei only exist for a short time before they continue to grow as grains or crystals and that these nuclei often form at defects or interfaces that are deeply buried in the bulk of the material. From the classical nucleation theory it is predicted that the energy of the interfaces that are involved in the nucleation process, i.e. the grain boundaries between the parent grains, and the interphase boundaries between the nucleus and matrix, are very important. In order to determine the energy of the interfaces the local atomic arrangement and chemistry should be known, which requires a local probe with atomic resolution. At the same time a large volume of the material needs to be probed in order to obtain good statistics about the different types of potential nucleation sites that are available in the heterogeneous microstructure of the alloy.

Moreover, the measurement of the grain boundary energy between parent grains should ideally be performed before the nucleus forms and the energy of the interface between the nucleus and the matrix should ideally be determined at the moment of the formation of a critical nucleus, which may only exist for a very short period of time.

Notwithstanding the great improvements and sophistication in experimental techniques, there is currently no technique available that fulfils the requirements described above. Studies of solid-state nucleation are nowadays limited to either high spatial resolution measurements with e.g. high-resolution electron microscopes and 3D-atom probes [1-3] or to measurements in which large volumes of the material are investigated with optical and electron microscopy [4], or to in-situ measurements with three-dimensional X-ray microscopes at synchrotron sources [5].

Despite the experimental difficulties, the theoretical framework of solid-state nucleation has continued to develop over the last decades. A large variety of solid-state nucleation models exist nowadays [6-11]. Different geometrical models have been developed for the shape of the critical nucleus and the role of grain and phase boundary misorientations. In one of the earlier models, Clemm and Fisher [12] assumed that the nuclei are composed of equivalent spherical caps. These nuclei appear at grain boundaries as symmetrical lenticular particles, at edges and corners with three or four spherical caps, respectively. The interfaces between the parent grains are assumed to be disordered, i.e. incoherent [13]. Clemm and Fisher calculated the activation energy for nucleation on the three above-mentioned locations and found that nucleation at grain corners is most favoured, followed by grain edges and grain faces. Homogeneous nucleation requires the most energy and is therefore the least favoured way for nucleation during solid-state phase transformations in the model of Clemm and Fisher.

The model of Clemm and Fisher has been used widely to describe the solid-state nucleation of ferrite in austenite. Lange et al. [4] experimentally studied ferrite nucleation on austenite grain faces in steel and found a very high nucleation rate for ferrite in the order of 250 to 500 nuclei per cm² of unreacted grain face area per second depending on the transformation temperature. To explain their experimental findings Lange et al. used several models for the nucleus shape. The spherical-cap based models, including the lenticular nucleus of Clemm and Fisher, together with the interface energies of the incoherent austenite/austenite grain boundaries and incoherent austenite/ferrite phase boundaries, could not explain this high nucleation rate. The model that could explain their experimental findings is the traditional disk-shaped ‘pillbox’ model, with all of its interfaces assumed to be partially or fully coherent and thus having a low interface energy. The coherent interfaces are assumed to be the result of a crystallographic orientation relationship between the ferrite nucleus and parent austenite grain. Lange et al. considered that the observation of a specific orientation relationship between two phases automatically implies the existence of a coherent phase boundary. In analogy with the pill-box model for grain faces, they developed coherent nucleus models for nucleation at grain edges and corners. However, due to the coherency requirement of these nuclei with three or four austenite grains at grain edges or corners, respectively, these nuclei are not expected to form often. As such, Lange et al. considered the pill-box model for nucleation at austenite grain faces to be even more dominant than nucleation at grain edges and corners. Later it was confirmed that by examining the macrotexture of steels before and after phase transformations the parent and product phases could be
related one-to-one with the use of the Kurdjumov-Sachs and/or Nishiyama-Wassermann orientation relationships [14, 15].

In a recent study [5], in-situ synchrotron measurements were carried out during the austenite/ferrite phase transformation in steel. In these experiments the ferrite nucleation rate was measured in real-time, but the location of the ferrite nuclei in the austenite matrix was not determined. These measurements showed that the coherent pillbox model in combination with the low interfacial energies as determined by Aaronson and co-workers could not be used to explain the temperature dependence of the nucleation rate that was observed experimentally. One possibility might be that there are possibly more favourable potential nucleation sites accommodating nuclei with different shapes and interfacial energies than provided by the coherent pillbox model.

This research is focused on the role of grain and phase boundary misorientations during solid-state ferrite nucleation in austenite. First, the influence of the misorientation of the austenite grain boundary on ferrite nucleation is studied to determine whether certain misorientations between austenite grains favour ferrite nucleation. Secondly, the present study intends to investigate the crystallographic misorientation between ferrite nuclei and surrounding austenite grains, focusing on ferrite nuclei formed on austenite grain faces. Thirdly, the effect of a slight deformation of the austenite matrix on the number of ferrite nuclei that form during isothermal annealing is investigated.

To this purpose, the crystallographic orientation of individual austenite and ferrite grains is measured by the Electron BackScatter Diffraction (EBSD) technique with orientation mapping (OIM) and phase identification (phase ID) tools, in both annealed and deformed material in order to study the effect of a small deformation on nucleation. In this work the exact 3D-location of nucleation could not be determined, because serial sectioning to obtain a 3D image of the microstructure was not performed. The 2D character of the measurements also obstructs the study of the inclination and therefore hinders the observation of coherency and the calculation of the interface energies of the grain boundaries. Nevertheless, the role of grain and phase boundary misorientations during solid-state nucleation of ferrite in austenite could be investigated with 2D-EBSD, as well as the effect of deformation on nucleation.

5.2 Experimental

5.2.1 Model alloy

In order to investigate the nucleation of ferrite in austenite, a structure that clearly reveals the ferrite nucleation stage, i.e. a partly transformed structure in the initial stage of transformation, is needed. In plain iron-carbon alloys austenite is not stable at room temperature. For this reason, an alloy in which both austenite and ferrite are stable at room temperature has to be used for the experiments. This means that the martensite start temperature ($M_s$) should be below room temperature. Also, the amount of ferrite present should be small, about 5 to 10%, to preserve the austenite grain structure and to determine the position at which the ferrite grain has nucleated.

Duplex stainless steels are a mixture of ferrite and austenite crystal structures. The primary alloying elements are carbon, chromium and nickel. The fraction of each phase is dependent on the composition and heat treatment. Most duplex stainless steels are intended to contain approximately equal amounts of ferrite and austenite phases in the annealed condition. With the appropriate annealing treatment the amount of ferrite can be varied. Unfortunately, carbon tends to form chromium carbides at austenite grain boundaries, which will influence the ferrite nucleation. It is aimed to exclude all factors that may affect the nucleation of the ferrite phase except grain boundaries. In order to obtain an alloy with a stable austenite structure at room temperature and a small portion of ferrite, a ternary iron-chromium-nickel alloy with 20 wt.% Cr and 12 wt.% Ni was chosen for this research and acquired from Goodfellow Cambridge Limited®. This alloy will be referred to as Fe-20Cr-12Ni henceforth.

The Fe-20Cr-12Ni alloy was made with Fe, Cr and Ni with purity >99.98 wt%. The metals were melted in an alumina crucible and cast into a round copper mould. Subsequently, the rod was further deformed by swaging at room temperature. The as-received material was homogenised at 1200°C for 10 hours. After homogenisation and quenching Electron Probe Micro-Analysis (EPMA) line scans showed that the elements are homogeneously distributed in the bulk material, whereas X-ray diffraction measurements revealed that only austenite is present in the homogenised alloy at room temperature.

5.2.2 Experiments

After the homogenisation treatment, the specimens were additionally reheated to 1400°C at a rate of 23°C/s, into the austenite/δ-ferrite region, with a Bähr 805 dilatometer, which was used because of the accuracy of its computer-controlled thermal unit. Three specimens were prepared. The first specimen was kept at 1400°C for 20 s and then rapidly cooled with He-gas to make sure that the partial γ → δ transformation was interrupted. The other specimens were kept at 1400°C for 100 s, and then subsequently quenched with He-gas to room temperature afterwards. During this heat treatment,
one of these specimens was slightly deformed with less than 0.2% deformation1. The heat-treated specimens were examined with XRD to determine the phases present and the spectra of both specimens showed that both austenite and ferrite were present after quenching. A summary of the heat treatments and specimens is given in Table 5-1.

Table 5-1: Parameters of the annealing treatments.

<table>
<thead>
<tr>
<th>Specimen name</th>
<th>Heat Treatment</th>
<th>Time (s)</th>
<th>Atm.</th>
<th>Cooling Rate</th>
<th>Deformation</th>
</tr>
</thead>
<tbody>
<tr>
<td>A20</td>
<td>23°C/s 1400°C</td>
<td>20</td>
<td>He, 3.7°C/s to 445°C, Q</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>A100</td>
<td>100 He, quenched (Q)</td>
<td>100</td>
<td>Vac.</td>
<td>He, quenched (Q)</td>
<td>No</td>
</tr>
<tr>
<td>D100</td>
<td>100 He, quenched</td>
<td>Yes, &lt; 0.2%</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Subsequently, the specimens were prepared for the EBSD measurements by mechanical (down to 1μm) and electrolytic polishing with Lectropol 5 equipment (electrolyte A2 (Struers'), flow rate 13, 25 s, 35 V).

The EBSD measurements for specimens A20 and D100 were carried out with an orientation imaging microscopy (OIM) system, which was installed on a FEI XL30 Environmental Scanning Electron Microscope (ESEM) with LaB6 filament. The EBSD patterns were acquired and analysed by means of the TSL OIM software. The microscopy settings for the EBSD measurements implied an acceleration voltage of 25 keV, a working distance of 19 mm, a spot size of 4.8, and a specimen tilt of 75°. In the analysis of the acquired data, only data points with a Confidence Index (CI) higher than 0.1 were considered. The step sizes of 0.5 and 0.6 μm in a hexagonal scan grid and a 4x4 binning were used for the EBSD measurements of the A20 and D100 specimen, respectively.

The EBSD measurement on specimen A100 was carried out with HKL Technology Channel 5 software installed on a FEI Nova 600 Nanolab Dual-Beam FIB SEM. In this orientation scan the following settings were used: an acceleration voltage of 20 keV, a working distance of 7 mm, a beam current of 2.4 nA and a specimen tilt of 70°. An area of 600x600 μm² was scanned with a square scan grid and a step size of 0.8 μm. The EBSD data were analysed by means of TSL OIM software.

5.3 Experimental results

The microstructures of the specimens are shown in Figure 5-1A, Figure 5-2A and Figure 5-3A for specimen A20, A100 and D100, respectively, by means of phase maps obtained with EBSD. The scans were recorded in the centre of the specimens. The average CI of the scans is 0.95 and 0.92 for specimens A20 and D100, respectively, and for specimen A100 the indexation rate was 97%, which indicates a very high reliability of the collected orientation data.

In the analysis, low angle grain boundaries (LAGBs) are defined as austenite grain boundaries with a misorientation angle between 1 and 15°, whereas high angle grain boundaries (HAGBs) are austenite boundaries with a misorientation angle between 15° and 62.8°, which is the maximum orientation distance between two cubic crystals [16]. In this paper a clear distinction is made between HAGBs and twin boundaries, where HAGBs are considered to be random high angle grain boundaries. In other words, in the analysis the values given for HAGBs only refer to grain boundaries with a misorientation of [15°-55°] and [60°-62.8°], in that way excluding twin boundaries.

1 The amount of deformation is determined from the dilatometer signal during the heat treatment.
The following specific orientation relationships between the FCC crystal lattice of the parent austenite and the BCC crystal lattice of the product ferrite are taken into account in the analysis of the EBSD maps: the Kurdjumov-Sachs (K-S), Nishiyama-Wassermann (N-W), Pitsch, and (inverse) Greninger-Troiano (G-T and G-T’) relationships [17]. However, the analysis software cannot distinguish the Pitsch and inverse Greninger-Troiano (G-T’) orientation relationships from the N-W and G-T orientation relationships, respectively [17]. The Miller index representations and the disorientation, i.e. the lowest possible angle found in all variants of a misorientation [18], in angle/axis pairs are listed in Table 5-2. The used tolerance for all orientation relationships is 2.5° around the disorientation angle.

The phase boundaries with a misorientation corresponding to one of the above mentioned orientation relationships are black. The microstructures display austenite grains with a diameter of 100 to 200 µm and a significant number of annealing twins. The presence of large austenite grains enhances the probability that the observed ferrite grains on the junction of two austenite grains in the 2D-EBSD images have in fact nucleated at grain faces and not at grain edges. In addition, it is very unlikely that an edge is straight over a long length and that the EBSD-section is exactly along this edge. In other words, the austenite grain boundaries observed in the EBSD scans are likely to be grain faces rather than grain edges.

In Figure 5-1B, Figure 5-2B and Figure 5-3B the Inverse Pole Figure orientation maps of the three specimens are shown. Figure 5-3C and D reveal the structure of the low angle grain boundary cells and the ferrite nuclei of specimen D100, encircled in Figure 5-3B. It shows that the spatial distribution of the ferrite grains corresponds strongly to the deformation sub-grain structure.

Table 5-2: Specific orientation relationships between FCC austenite and BCC ferrite, represented by Miller indices of the corresponding crystal planes and directions and by the axis/angle pair of the crystal misorientation.

<table>
<thead>
<tr>
<th>Orientation Relationship</th>
<th>Representation</th>
<th>Disorientation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kurdjumov-Sachs</td>
<td>{1 1 1}, //{0 1 1}, {&lt;1 0 1&gt;, //{1 1 1}_a</td>
<td>42.8°/&lt;2 2 11&gt;</td>
</tr>
<tr>
<td>Nishiyama-Wassermann</td>
<td>{1 1 1}, //{0 1 1}, {&lt;1 1 2&gt;, //{0 1 1}_a</td>
<td>45.98°/&lt;2 5 24&gt;</td>
</tr>
<tr>
<td>Pitsch</td>
<td>{0 1 0}, //{1 0 1}, {&lt;1 0 1&gt;, //{1 1 1}_a</td>
<td>45.98°/&lt;5 2 24&gt;</td>
</tr>
<tr>
<td>Greninger-Troiano</td>
<td>{1 1 1}, //{0 1 1}, {&lt;5 12 17&gt;, //{7 17 17}_a</td>
<td>44.23°/&lt;3 2 15&gt;</td>
</tr>
<tr>
<td>Inverse Greninger-Troiano</td>
<td>{5 12 17}, //{7 17 17}, {&lt;1 1 1&gt;, //{0 1 1}_a</td>
<td>44.23°/&lt;2 3 15&gt;</td>
</tr>
</tbody>
</table>

From the orientation maps the misorientations between the austenite grains can be determined and the area-fractional distribution in terms of misorientation is plotted in Figure 5-4A for all specimens. The angular accuracy of orientation measurements is typically 1° [19, 20] and therefore 1° is taken as the minimum misorientation angle. The columns in the discrete plot represent intervals of 5° of misorientation, which is well in excess of the angular accuracy of the measurements. The group of high angle grain boundaries consist of random high angle grain boundaries (further called HAGBs), twin boundaries and CSL boundaries. The area-fractional distribution plots of specimens A20 and A100 show that ~70-80% of all grain boundaries fall in the interval of the [55°-60°] misorientation, which contains the well-known twin misorientation with an angle/axis pair of 60°/<1 1 1>. From the EBSD-measurements it is found that more than 90% of the boundaries with a misorientation of ~60° are twin boundaries for all specimens. Furthermore, only very small fractions of 28 possible CSL boundaries (S5 to S35b) are present in all three specimens, in total 1.3%, 0.4% and 0.5% for A20, A100 and D100, respectively. From this we can conclude that the high angle grain boundary group mainly consists of random HAGBs and twin boundaries.
Figure 5-4: Discrete plots of A) the distribution of grain boundary misorientation angles in the austenite phase; B) the number of ferrite grains per unit area of austenite grain face per misorientation class. Each column represents the average per 5 degrees of misorientation and includes the statistically absolute error. The annealed specimens have no austenite grain boundaries in the interval \(1°-5°\). The deformed specimen has no grain boundaries in the interval \(10°-15°\). The twins in all three specimens have a rotation angle of ~59.8° and are included in the \(55°-60°\) interval.

To investigate how ‘efficient’ the grain boundaries were in acting as ferrite nucleation sites, the number of ferrite nuclei \(N_a\) per unit area of unreacted austenite grain face area\(^2\) per austenite grain boundary interval is shown in Figure 5-5. The numbers plotted in this graph are shown in Table 5-3, along with the parameters needed to calculate \(N_a\) from the experimental data. The number distribution of ferrite nuclei per unit area of unreacted austenite grain face is calculated according to the Schwartz-Saltykov analysis \([4, 21, 22]\):

\[
N_a = \frac{1}{\Delta} \sum_{i} \alpha_i \eta_i
\]

where \(\Delta\) is the interval size obtained by dividing the largest observed diameter of a ferrite grain in the entire microstructure by the number of size groups \(k\), \(\eta_i\) is the number of

\[\text{Unreacted austenite grain face area refers to the austenite grain face that is retained after nucleation and growth of the ferrite grains.}\]

Furthermore, specimens A20 and A100 do not contain any LAGBs with \(\left[1°-5°\right]\) misorientation and specimen A100 also does not contain any LAGBs with \(\left[5°-10°\right]\) misorientation. Specimen D100 contains more than 50% of grain boundaries with \(\left[1°-5°\right]\) misorientation and 25% of grain boundaries with \(\left[55°-60°\right]\) misorientation.

In Figure 5-4B the number of observed ferrite grains is plotted versus the misorientation angle of the austenite grain boundary on which they have nucleated. Coinciding for specimens A20 and A100, most ferrite grains are found in the interval \(\left[55°-60°\right]\). Only a few ferrite grains were found on grain boundaries with a misorientation of \(\left[60°-65°\right]\) for these specimens. The plot of specimen D100 shows that most ferrite grains appear in the intervals \(\left[1°-5°\right]\) and \(\left[55°-60°\right]\). No ferrite grains were found on grain boundaries with a misorientation of \(\left[10°-15°\right]\). The number of ferrite grains found in specimens A20 and A100 was only about one third of the amount found in specimen D100.
ferrite grains per unit length of unreacted austenite grain boundary\(^3\) per size group and \(a_i\) are the tabulated coefficients which reflect the stereological shape factor due to a two-dimensional section of three-dimensional spheres [22, 23], different for each size group.

Due to the limited number of ferrite grains present at grain faces in the EBSD scans, i.e. 142, 140 and 283 for specimen A20, A100 and D100, respectively, the number of size groups was chosen to be the smallest that was reasonably possible for statistical purposes, i.e. \(k = 7\) [22]. The distribution over different size groups is necessary for the correct presentation of the number of ferrite grains per unit area of unreacted austenite grain face, as the shape factors change for each size group. The austenite grain boundary groups were chosen to represent intervals with distinct characteristics, i.e. LAGB, HAGB, and twins. The number of observed ferrite grains in each size group and grain boundary misorientation interval is given in Table 5-3, which shows that some intervals contain no ferrite grains or only a small number, indicating the limited statistics in this analysis.

The argument to use the unreacted grain boundary length is that this parameter is easily extracted from the EBSD data, whereas the total amount of austenite grain boundary length must be conjectured by reconstructing the former austenite grain boundary.

---

### Table 5-3: Number of ferrite grains per unit area of unreacted austenite grain face (\(N_A\)) per austenite grain boundary group. The entire population of austenite grains is divided in \(k\) size classes of equal size \(\Delta\) and in three misorientation classes corresponding to LAGBs, random HAGBs and twins. The statistical absolute error of \(N_A\) is given as well.

<table>
<thead>
<tr>
<th>Size groups (k)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>Total (a)</th>
<th>(\gamma) GB Length ((\mu)m)</th>
<th>(\Delta)</th>
<th>(N_A) ((\mu)m(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>LAGB (1-15°)</td>
<td>9</td>
<td>3</td>
<td>3</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>16</td>
<td>936</td>
<td>6.7</td>
<td>1.80*10(^{-3})</td>
<td>±3.51*10(^{-4})</td>
</tr>
<tr>
<td>HAGB (15-65°)</td>
<td>49</td>
<td>19</td>
<td>13</td>
<td>5</td>
<td>1</td>
<td>1</td>
<td>89</td>
<td>3160</td>
<td>5.68*10(^{-4})</td>
<td>±7.68*10(^{-5})</td>
<td></td>
</tr>
<tr>
<td>Twin (Σ 3)</td>
<td>26</td>
<td>9</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>39</td>
<td>8040</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LAGB (1-15°)</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>3</td>
<td>83</td>
<td>6.16*10(^{-3})</td>
<td>±4.24*10(^{-3})</td>
<td></td>
</tr>
<tr>
<td>HAGB (15-65°)</td>
<td>42</td>
<td>30</td>
<td>8</td>
<td>4</td>
<td>1</td>
<td>1</td>
<td>87</td>
<td>1439</td>
<td>1.28*10(^{-2})</td>
<td>±1.54*10(^{-3})</td>
<td></td>
</tr>
<tr>
<td>Twin (Σ 3)</td>
<td>21</td>
<td>14</td>
<td>5</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>46</td>
<td>7611</td>
<td>1.22*10(^{-4})</td>
<td>±2.05*10(^{-4})</td>
<td></td>
</tr>
<tr>
<td>LAGB (1-15°)</td>
<td>99</td>
<td>17</td>
<td>6</td>
<td>4</td>
<td>2</td>
<td>1</td>
<td>130</td>
<td>4034</td>
<td>5.82*10(^{-3})</td>
<td>±5.43*10(^{-4})</td>
<td></td>
</tr>
<tr>
<td>HAGB (15-65°)</td>
<td>70</td>
<td>6</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>78</td>
<td>1737</td>
<td>9.05*10(^{-3})</td>
<td>±1.05*10(^{-3})</td>
<td></td>
</tr>
<tr>
<td>Twin (Σ 3)</td>
<td>51</td>
<td>10</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>64</td>
<td>1750</td>
<td>6.87*10(^{-3})</td>
<td>±8.96*10(^{-4})</td>
<td></td>
</tr>
</tbody>
</table>

The number of ferrite grains per unit area unreacted austenite grain face \(N_A\) for specimen A20 and A100 shows that \(N_A\) for HAGBs is significantly higher than for LAGBs and that \(N_A\) for LAGBs is higher than for twins. The plot for specimen D100 shows the highest \(N_A\) for HAGBs, followed by \(N_A\) for twin boundaries and LAGBs. Comparing the annealed (A20 and A100) and deformed (D100) specimens it is observed that \(N_A\) for
twin boundaries is ten to twelve times higher for specimen D100, and \( N_f \) for LAGBs and HAGBs are three times higher after deformation. Specimen A100 has a very large error bar for LAGBs and the lower limit of the value of \( N_f \) is also three times smaller than the lowest value of \( N_f \) for specimen D100. The reason that \( N_f \) for HAGBs for specimen A100 is larger than the other ones can probably be attributed to the fact that the ferrite grains in this specimen are larger due to a longer annealing time.

In Figure 5-6 the distribution of phase boundary fractions of all three specimens are shown in a discrete plot. It is clearly observed that the maximum phase boundary fraction of all three specimens lie in the interval of [40-50°]. This disorientation interval contains all specific FCC-BCC orientation relationships, which runs from 40.4° for the Kurdjumov-Sachs orientation relationships to 48.5° for the Nishiyama-Wassermann and Pitsch orientation relationships, with a tolerance of 2.5°. Approximately 80% (A20 and A100) and 90% (D100) of all phase boundaries can be found in this misorientation interval.

![Figure 5-6: Discrete plot displaying the distribution of misorientation angles between the austenite and ferrite phases, i.e. the phase boundaries. In this figure all ferrite grains were taken in consideration. Each column represents the grain boundary fraction per 10 degrees of misorientation and includes the statistical absolute error.](image)

In Figure 5-7 the division of ferrite grains with and without a specific orientation relationship (OR) with one of the surrounding austenite grains is shown, together with the subdivision of nucleation within an austenite grain, on faces and at triple junctions. The grain faces are subsequently divided into high and low angle grain boundaries (HAGBs and LAGBs, respectively). The HAGBs are subdivided in twin boundaries, 60°/<1 1 1>, also known as \( \Sigma 3 \) boundaries, Coincidence Site Lattice (CSL) boundaries and random HAGB. The ferrite grains on austenite grain faces with an OR are also divided in having an OR all around (all OR) or with only one austenite grain (1 side). The rest of the ferrite grains display a partial OR around their circumference.

The tolerance of the misorientation of the investigated CSL boundaries is defined by the correspondence \( K/2\ell \). For the constants \( K \) and \( \ell \) the values of the Palumbo-Aust criterion is used, i.e. \( K = 15 \) and \( \ell = 5/6 \). The Palumbo-Aust criterion is more restrictive than the widely accepted Brandon criterion, because it reduces the fraction of grain boundaries counted as special but displaying non-special behaviour [24]. LAGB and twin boundaries (\( \Sigma 1 \) and \( \Sigma 3 \), respectively) were investigated separately. To obtain the results of Figure 5-7, all ferrite grains visible in the EBSD scans for each specimen have been considered. The observations made from Figure 5-7 are listed below. The sequence of listed figures always corresponds to the order A20, A100 and D100, respectively.

- 29.2%, 23.2% and 22.8% of all observed ferrite grains have nucleated at triple junctions, i.e. at grain edges or corners.
- 64.8%, 48.8%, and 47.1% of all observed ferrite grains have nucleated at grain faces
- 5.9%, 27.5% and 30.1% of all observed ferrite grains were observed within an austenite grain, suggesting intra-granular nucleation.
- 89.0%, 87.1% and 85.4% of all observed ferrite grains have an orientation relationship with at least one of the neighbour grain faces and at least along part of the phase boundary.

Observations related to ferrite nucleation on austenite/austenite grain faces:

- 8.2%, 6.6% and 4.2% of all observed ferrite grains have formed on incoherent grain boundaries with incoherent phase boundaries, which can be related to the theory of Clemm and Fisher.
- 6.4%, 6.6% and 20.2% of all observed ferrite grains have formed on twin or LAGBs with a phase boundary that has an orientation relationship around the full circumference of the nucleus, which can be related to the coherent pillbox model.
• 32.8%, 19.1% and 14.0% of all observed ferrite grains have formed on twins or LAGBs with a phase boundary that has an orientation relationship on one side of the nucleus, which can be related to the pillbox-cum-spherical-cap nucleation models of Aaronson and co-workers.

• The remaining ferrite grains, 14.6%, 10.5% and 3.7%, display orientation relationships with the austenite grain along part of the interphase.

When looking at the ‘efficiency’ ($N_A$) of grain boundaries in acting as ferrite nucleation sites, it is found that for all specimens random HAGBs are slightly preferred for nucleation. Because nucleation obviously takes place at all kinds of austenite grain boundaries, several mechanisms for ferrite nucleation must be active, amongst them nucleation according to the theory of Clemm and Fisher and the coherent pillbox model. The nucleation theory of Clemm and Fisher assumes that ferrite will nucleate on random high-angle grain faces, edges and corners without any orientation relationship between the ferrite nucleus and the austenite matrix and thus with incoherent phase boundaries. The results in Figure 5-7 show that for specimen A20 8.2%, for specimen A100 6.6% and for specimen D100 4.2% of the ferrite grains nucleate without an orientation relationship on a random HAGB or on a triple junction.

In case ferrite nucleation takes place according to the coherent pillbox model, ferrite grains should appear at special boundaries such as Coincidence Site Lattices (CSLs), of which the twin boundary is an example, and with an orientation relationship with the austenite matrix around the whole circumference of the ferrite grain. Figure 5-7 shows that 6.4% of the ferrite grains in specimen A20, 6.6% for specimen A100 and 20.2% of the ferrite grains in specimen D100 have an orientation relationship around the whole circumference and lie on a special austenite boundary.

The reason why much more ferrite grains have nucleated in the deformed specimen than in the annealed specimens is due to the presence of low angle grain boundaries (LAGBs) in the deformed specimen, which are candidates for the coherent pillbox nucleation mechanism as well, because their small misorientations imply semi-coherency between the parent grains. For the deformed specimen the LAGBs with a misorientation of $|1^\circ - 5^\circ|$ are present in abundance, but are difficult to investigate with EBSD, because of the limited angular accuracy. As some of the LAGBs exhibited a misorientation which was lower than $1^\circ$ they were not taken into account in the present study and hence a number of ferrite nuclei were considered as intra-granular nuclei and do not appear in the LAGB column of the deformed specimen in Figure 5-4B. By consequence, it is very well plausible that the number of nuclei in the low-angle domain has been underestimated in the calculated value shown in Table 5-3.
For more than 75% of the ferrite grains the models of Clemm and Fisher and the coherent pillbox model cannot explain the nucleation mechanism. Figure 5-6 shows that most interphases have a specific orientation relationship between the ferrite nucleus and the austenite matrix and that 30 to 40% of the ferrite grains display a specific orientation relationship with at least one of the surrounding austenite grains. A somewhat more developed variant of the pill-box model assumes a (coherent) pill-box interface topped with an (incoherent) spherical cap, i.e. the pill-box-cum-spherical-cap (PCSC) nucleus model [4] having one incoherent spherical cap lying within the matrix grain or in line with the grain boundary. A schematic representation of these PCSC-models and the corresponding experimental observations in the specimens are shown in Figure 5-8. Both the coherent and semi- incoherent pillbox models could explain the experimentally observed ferrite nucleation rates as observed by Aaronson and co-workers, but they chose the coherent pillbox model as the mechanism by which ferrite nucleation takes place on the basis of experimental observations of King and Bell [25]. However, this work shows that ferrite nucleation not only takes place via the coherent pillbox mechanism, but also via the PCSC and other mechanisms.

![Figure 5-8: Examples of A) nucleation according to the coherent pillbox model on a twin boundary (green) with a ferrite grain having an orientation relationship with both austenite grains; B) pillbox-cum-spherical cap model on a random HAGB (grey), having an orientation relationship with only one austenite grain. The spherical cap is situated on the bottom of the pillbox, in line with the austenite grain boundary; C) intra-granular nucleation with the ferrite grain having an orientation relationship (black) all around the circumference; D) nucleation according to the pillbox-cum-spherical cap model on a random HAGB (grey), having an orientation relationship with only one austenite grain. The spherical cap is situated on top of the pillbox. The background colours refer to the IPF map and legend in Figure 5-3.](image)

Figure 5-7 shows that the pillbox-cum-spherical cap models can explain the experimentally observed nucleation process for 32.8%, 18.8% and 14% of the ferrite grains for specimen A20, A100 and D100, respectively. It was assumed by Aaronson et al. [4] that an orientation relationship between two phases automatically leads to a coherent phase boundary. However, an orientation relationship is usually described as an angle/axis pair, which defines the relationship between the two neighbouring grains and not the position of the interface itself. The interface could be inclined at any angle within the interpenetrating lattices [18] and therefore the degree of coherency could change with any inclination angle used. When the coherency assumption is discarded and it is assumed that the caps can also represent incoherent phase boundaries with a special OR, this explains an additional 3.7%, 2.8% and 2.0% of all ferrite nuclei.

In total, the coherent pillbox model and the PCSC model with and without the coherency constraint can explain 42.9, 28.2% and 36.2% of the experimentally observed ferrite nuclei for specimens A20, A100 and D100, respectively. When only the ferrite nuclei on austenite grain faces are taken into account, around 60 to 75% of these ferrite grains will have nucleated according to the above mentioned mechanisms.

Of all ferrite grains, 5.9%, 27.5% and 30.1% for specimens A20, A100 and D100, respectively, were observed within an austenite grain, suggesting intragranular nucleation or nucleation on LAGBs. It seems obvious that all of these grains should have an orientation relationship with the surrounding austenite. However, a small part does not correspond to any of the specific relationships of Table 5-2. Because of the limitations of the experimental technique to 2D observation, it is also possible that part of these grains do nucleate on grain boundaries or triple junctions, which cannot be observed, i.e. the nucleation point is situated under the observation plane and the observed ferrite grain contacts with different neighbours outside the observation plane. Therefore an EBSD investigation combined with serial sectioning, which allows 3D reconstruction of the microstructure, could be a successful step to establish whether intragranular nucleation really occurs.

Out of all ferrite grains 31.2%, 23.3% and 22.8% are located at triple junctions for specimens A20, A100 and D100, respectively. The remaining ferrite grains have an orientation relationship with the surrounding austenite along part of the phase boundary, i.e. 14.6%, 10.5% and 3.7% of the ferrite grains in specimens A20, A100 and D100, respectively.

As the deformation in specimen D100 had a large influence on the microstructure and the number of ferrite grains nucleated in the specimen, the question arises whether the deformation actually contributed to the increased ferrite nucleation. Comparing specimens A100 and D100, which were both annealed at 1400°C for 100s, omitting deformation for specimen A100, it is clear that the high number of ferrite grains cannot
be attributed to the increased annealing time. Specimen A100 displays approximately the same number of ferrite grains in the specimen as specimen A20, which was only kept for 20 s at 1400°C. No other variables of the annealing treatment were changed, which lead to the observation that the deformation of less than 0.20% of specimen D100 has produces the increased amount of nucleated ferrite grains.

When all specimens are compared, it is observed that in the deformed specimen a high density of LAGBs in the interval [1°-5°] is present, and LAGBs in this interval are not present in specimens A20 and A100, cf. Figure 5-4. The remarkable similarities in the cellular structure of the LAGBs and the ferrite nuclei, as revealed in Figure 5-3C and D, show that these LAGBs have played an important role as ferrite nucleation sites in the deformed material. This phenomena was also observed by Lacroix and Bréchet et al. [26, 27]. These LAGBs, which accommodate the orientation difference between different zones of a grain, largely enhance nucleation according to the coherent pillbox model, since most of the ferrite nuclei on these LAGBs have an orientation relationship around their full circumference.

In summary, several mechanisms for ferrite nucleation are active, amongst them nucleation according to the theory of Clemm and Fisher, the coherent pillbox model and the pillbox-cum-spherical cap models. It seems that when the assumptions on automatic coherency in combination with an orientation relationship are discarded, the pillbox-cum-spherical cap models can explain a large part of the observed ferrite nucleation for all three specimens. However, the EBSD-measurements are not sufficient to explain the small activation energy for nucleation found from synchrotron radiation measurements [5], because information about the 3D microstructure is not available.

5.5 Conclusion

The roles of grain and phase boundary misorientations during nucleation of ferrite in austenite have been investigated, as well as the effect of a slight deformation of the austenite matrix on the density of ferrite nuclei that form during subsequent isothermal annealing. Two specimens are annealed for 20 and 100 s at 1400°C. One specimen is slightly deformed and subsequently annealed for 100 s at 1400°C.

We observed that almost 90% of all observed ferrite grains in the three specimens have a specific orientation relationship with at least one austenite grain or at least along part of the phase boundary, which implies that the specific orientation relationship plays an important role during solid-state nucleation of ferrite.

Ferrite nucleation is observed at triple junctions (grain edges or corners), at grain faces, and within a grain (intragranular nucleation). Experimentally we observed that approximately half of the ferrite grains have nucleated at grain faces.

In the specimen that was slightly deformed during annealing for 100 s, three times more ferrite grains were observed in the bulk of the material compared to the specimen that was annealed for 100 s without imposed plastic deformation. The observed LAGB structure in the deformed specimen is induced by the deformation and not by the nucleation process itself because the nucleation of ferrite grains during annealing at 20 and 100 s does not lead to the formation of additional low-angle grain boundaries, in the absence of externally imposed plastic strain.

We observed that ferrite nucleation on austenite/austenite grain faces with random high-angle grain boundaries is slightly more efficient than nucleation on low-angle grain boundaries and twin boundaries. During ferrite formation at grain faces, three different types of nucleation mechanisms are simultaneously active which can be related to the theory of Clemm and Fisher, the coherent pillbox model, and the pillbox-cum-spherical-cap model.

5.6 Acknowledgements

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5.7 References


The role of crystallographic misorientations during nucleation of BCC grains on FCC grain boundary faces in Co-15Fe studied by 3D-EBSD
6. The role of crystallographic misorientations during nucleation of BCC grains on FCC grain boundary faces in Co-15Fe studied by 3D-EBSD

6.1 Introduction

Understanding the grain nucleation mechanism during solid-state phase transformations in polycrystalline materials is a long-standing problem in the field of materials science. The nucleation stage has a strong influence on the overall kinetics of phase transformations and recrystallization processes. This determines the final microstructure and thereby the mechanical properties of the material. The understanding of grain nucleation is important for controlling the production process, the design of new alloys with optimal mechanical properties, and the production of tailor-made alloys.

During solid-state phase transformations heterogeneous nucleation takes place on grain boundaries, as it is well known that they act as preferential nucleation sites [1, 2]. The experimental difficulty in the study of solid-state nucleation is caused by the fact that the critical nuclei only exist for a short time before they continue to grow as grains or crystals and that these nuclei often form at defects or interfaces in the bulk of the material. From the classical nucleation theory it is known that the energy of the interfaces that are involved in the nucleation process, i.e. the grain boundaries between the parent grains and the interphase boundaries between the nucleus and matrix are very important.

The activation energy for heterogeneous nucleation $\Delta G_{het}^*$ is defined as

$$\Delta G_{het}^* = \frac{4}{27} \sum_{i} \left( \frac{\Delta G_i}{\sigma_i} \right)^2$$

where $\sigma_i$ represents the interface free energies of all interfaces, $\Delta G_i$ is the difference in volume free energy of the phases involved, $\Delta G_i$ is the misfit strain energy per unit volume, $z_i^*$ is a geometrical parameter depending on the shape of the $i^{th}$ interface and $z_V$ is a geometrical parameter depending on the shape of the nucleus [3]. The coefficient $z_i^*$ can be positive and negative for forming and disappearing interfaces, respectively. From this equation it is clear that the interface free energies and therefore the misorientations of the grains involved play a large role in the nucleation process.

Theoretical considerations by Clemm and Fisher [2] show that the activation energy for nucleation decreases for nuclei appearing at incoherent high angle grain boundary faces, edges and corners respectively. A grain boundary corner (GBC) is defined as a point where four parent grains meet, a grain boundary edge (GBE) as a line where three parent grains meet, and a grain boundary face (GBF) as a face where two parent grains meet. In this theory it is assumed that the boundaries between grains of the parent and boundaries between the matrix and the nucleus are incoherent. Furthermore, it is assumed that the geometry of the nucleus consists of spherical caps. The interface energy is assumed to be isotropic and specific orientation relationships (OR) between the parent and product phases are not taken into consideration.

In another study [4] ferrite nucleation on austenite grain faces in steel was experimentally studied and a very high nucleation rate for ferrite was found. These experimental findings could not be explained by the spherical-cap based models, together with the interface energies of the incoherent austenite/austenite grain boundaries and incoherent austenite/ferrite phase boundaries. The model that could explain this high nucleation rate is the traditional disk-shaped ‘pillbox’, with all of its interfaces assumed to be partially or fully coherent and thus having low interface energy. In order to form a coherent interface between the nucleus and the matrix two requirements need to be fulfilled: 1) a specific crystallographic orientation relation between the nucleus and the matrix and 2) the spatial orientation of the interface should be such that the atomic planes of the nucleus match with the atomic planes of the matrix at the position of the interface.

To describe the structure of a grain boundary between two crystals at least five macroscopic parameters are needed [5, 6]. These parameters are the three descriptors of the grain boundary misorientation, which are angle $\theta$ and $U, V$ from the axis direction $<U\bar{V}W>$, and the two descriptors of the grain boundary inclination, i.e. the direction of the grain boundary plane, $\Phi_x$ and $\Phi_z$:

$$\sigma = f(\theta, U, V, \Phi_x, \Phi_z)$$

Other parameters are pressure $P$ and temperature $T$, which are usually stated, and impurity levels $C_i$, which is frequently assumed to be zero. In addition to these five macroscopic parameters there are three microscopic parameters on the atomic scale that refer to translations on the atomic level to minimize the interface free energy. They are difficult to measure or to manipulate and do not contribute to distinguish between interface energies. This leaves the number of parameters to describe the grain boundary structure to five. In turn the misorientation and inclination depend on the
crystallographic orientations of the grains involved as these determine the amount of excess free energy and atomic disorder in the grain boundary region.

In the case of a grain boundary face (GBF) three main categories of grain boundary misorientation that play a large role in the research of solid-state nucleation, can be distinguished [2, 4, 7]: low-angle grain boundaries (i.e. $\theta < 15^\circ$) (LAGB), coherent twin boundaries ($\langle 1 1 1 \rangle$) and high-angle grain boundaries (i.e. $\theta \geq 15^\circ$) (HAGB). Low-angle grain boundaries and coherent twin boundaries have a low grain boundary energy, which can be calculated in particular cases according to the dislocation models [8]. The variation of energy with misorientation of high-angle grain boundaries has been investigated [9] as well as the variation of energy with inclination of phase boundaries [10]. From these investigations it became clear that the interface free energy curve shows local minima, i.e. cusps, when the misorientation or the inclination angle is varied.

Table 6-1: Representations and disorientations of the investigated orientation relationships.

<table>
<thead>
<tr>
<th>Orientation Relationship</th>
<th>Representation</th>
<th>Disorientation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kurdjumov-Sachs</td>
<td>$\langle 1 1 1 \rangle//\langle 0 1 1 \rangle$, $\langle 1 1 0 \rangle//\langle 1 1 1 \rangle$</td>
<td>$42.8^\circ//\langle 2 2 11 \rangle$</td>
</tr>
<tr>
<td>Nishiyama-Wasserman</td>
<td>$\langle 1 1 1 \rangle//\langle 0 1 1 \rangle$, $\langle 1 1 2 \rangle//\langle 0 1 1 \rangle$</td>
<td>$45.98^\circ//\langle 5 2 24 \rangle$</td>
</tr>
<tr>
<td>Pitsch</td>
<td>$\langle 0 1 1 \rangle//\langle 1 1 1 \rangle$, $\langle 1 1 1 \rangle//\langle 1 1 1 \rangle$</td>
<td>$44.23^\circ//\langle 3 2 15 \rangle$</td>
</tr>
<tr>
<td>Greninger-Troiano</td>
<td>$\langle 1 1 1 \rangle//\langle 0 1 1 \rangle$, $\langle 5 12 17 \rangle//\langle 7 17 17 \rangle$</td>
<td>$44.23^\circ//\langle 2 3 15 \rangle$</td>
</tr>
<tr>
<td>Inv. Greninger-Troiano</td>
<td>$\langle 5 12 17 \rangle//\langle 1 1 1 \rangle$, $\langle 0 1 1 \rangle//\langle 1 1 1 \rangle$</td>
<td>$44.23^\circ//\langle 2 3 15 \rangle$</td>
</tr>
</tbody>
</table>

It was suggested [4] and reported [11, 12] that BCC grains at GBFs have a specific OR with at least one of the adjacent FCC matrix grains, i.e. the Kurdjumov-Sachs (K-S) or Nishiyama-Wasserman (N-W) orientation relationship. The other reported ORs, Pitsch [13], Greninger-Troiano [14] and inverse Greninger-Troiano [12], are also included in this study. These specific orientation relationships are listed in Table 6-1.

It has been found that between different variants of the Kurdjumov-Sachs (KS) orientation relationship 10 misorientation angles are possible, i.e. $10.5^\circ$, $14.9^\circ$, $20.6^\circ$, $21.1^\circ$, $47.1^\circ$, $49.5^\circ$, $50.5^\circ$, $51.7^\circ$, $57.2^\circ$ and $60^\circ$ [15], which are listed in Table 6-2.

Table 6-2: Possible misorientations between different variants, arising from one single parent grain, according to the Kurdjumov-Sachs orientation relationship.

<table>
<thead>
<tr>
<th>Angle (°)</th>
<th>U</th>
<th>V</th>
<th>W</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.5</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>10.5</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>14.9</td>
<td>6</td>
<td>1</td>
<td>16</td>
</tr>
<tr>
<td>20.6</td>
<td>-11</td>
<td>-6</td>
<td>11</td>
</tr>
<tr>
<td>21.1</td>
<td>7</td>
<td>-15</td>
<td>17</td>
</tr>
<tr>
<td>47.1</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

Between the different variants of the Nishiyama-Wassermann (NW) orientation relationship 5 misorientation angles are possible, i.e. $13.8^\circ$, $19.5^\circ$, $50^\circ$, $53.7^\circ$ and $60^\circ$ [16], which are listed in Table 6-3. These misorientations are independent of the parent and product phases, i.e. are valid for both FCC and BCC variants.

Most of the studies on the nucleation behavior of the BCC phase in the FCC phase were done with 2D-EBSD [7, 11] in which only three parameters, i.e. the angle/axis pair, of the misorientations of FCC grain boundaries and FCC/BCC phase boundaries are included. The important advantages of 3D-EBSD over 2D-EBSD are: 1) a distinction can be made between grain corners, edges, and faces, which is important to characterize the type of potential nucleation site, 2) the spatial orientation of the interface between two grains can be determined with respect to the crystal orientation of the grains, and 3) a distinct can be made between multiple nuclei with the same crystallographic orientation and one nucleus with a branched geometry.

Table 6-3: Possible misorientations between different variants, arising from one single parent grain, according to the Nishiyama-Wassermann orientation relationship.

<table>
<thead>
<tr>
<th>Angle (°)</th>
<th>U</th>
<th>V</th>
<th>W</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.8</td>
<td>1</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>19.5</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>50.0</td>
<td>-17</td>
<td>13</td>
<td>-17</td>
</tr>
<tr>
<td>53.7</td>
<td>-18</td>
<td>-19</td>
<td>6</td>
</tr>
<tr>
<td>60</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

The aim of this research is to investigate the role of crystal misorientations during...
nucleation of BCC-grains on FCC-GBF. In order to promote the understanding of nucleation mechanism at GBFs, it is necessary to examine the crystallography of BCC grains in three dimensions. The precipitation behavior at GBFs is examined in detail for an FCC (matrix)-BCC (grain) system focusing on the crystallography of the grains comprising the GBFs and the OR between BCC grains and the two adjacent FCC matrix grains.

6.2 Experimental

To study the solid-state nucleation of the BCC phase in the FCC phase, a structure that clearly reveals the location of the BCC nuclei with respect to the parent phase is needed, i.e., a partly transformed structure in the initial stage of transformation. In plain Fe–C alloys austenite (FCC) is not stable at room temperature. For this reason, an alloy in which both the FCC and BCC phases are stable at room temperature has to be used for the experiments. To this purpose a Co-15Fe alloy is used. The chemical composition of the alloy is given in Table 6-4.

Table 6-4: Chemical composition of alloy used (mass %).

<table>
<thead>
<tr>
<th>Element</th>
<th>Co</th>
<th>Fe</th>
<th>Ni</th>
<th>C</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percentage (mass %)</td>
<td>84.6</td>
<td>14.7</td>
<td>0.39</td>
<td>0.002</td>
<td>0.014</td>
</tr>
</tbody>
</table>

In order to study the crystallographic orientation relations between the BCC and FCC phases and the locations in the parent structure at which the nucleus most likely formed the Co-15Fe alloy was used to create a microstructure with small BCC grains or grains that nucleated at the grain boundaries of large FCC grains. The FCC and BCC phases are both stable at room temperature, which makes it possible to study the microstructure in three-dimensions (3D) by means of serial sectioning in combination with SEM and EBSD.

The alloy was heated for 30 min at 1273K, subsequently cooled to 973K, and was held at this temperature for 24 hours. During isothermal aging at 973K, the BCC phase precipitated from the supersaturated FCC matrix. As a result the FCC grains are relatively large compared to the BCC grains, as the FCC grains have a diameter of 50-100 μm and the BCC grains 0.1-1 μm. The combination of large FCC parent grains and small BCC product grains is very helpful in determining the type of potential nucleation site at which the grains actually nucleated, e.g. grain corner, edge, or face. In addition, it is important to have large FCC grains, because it cannot be avoided that the BCC grains grow after nucleation. A disadvantage is that large grains require a larger area to be scanned to find enough grains for statistical analysis.

The microstructures were examined by scanning electron microscopy (SEM) and electron backscatter diffraction (EBSD). In order to study large surface areas mechanical polishing outside the electron microscope was chosen instead of FIB, which is suited for smaller volumes. The sequential EBSD maps that were recorded could be positioned with respect to each other with a precision of approximately 10 μm. This is due to the mechanical polishing outside the electron microscope and the repositioning afterwards in the electron microscope. The inaccuracy in positioning the EBSD maps with respect to each other is too large in comparison to the size of the BCC grains (0.3 to 5 μm) and the distance between the BCC grains to be able to determine which cross-sections of the BCC grains that are taken at different depths in the material belong to one and the same BCC grain. In addition, the inaccuracy in positioning the EBSD maps means that the determination of the parameters $\Phi_y$ and $\Phi_z$ of the inclination of the grain boundary face could not be performed.

Table 6-5: Distances between the EBSD maps.

<table>
<thead>
<tr>
<th>EBSD map</th>
<th>Distance (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1-E2</td>
<td>2.78</td>
</tr>
<tr>
<td>E2-E3</td>
<td>0.8</td>
</tr>
<tr>
<td>E3-E4</td>
<td>1.46</td>
</tr>
<tr>
<td>E4-E5</td>
<td>3.64</td>
</tr>
<tr>
<td>E5-E6</td>
<td>4.86</td>
</tr>
<tr>
<td>E6-E7</td>
<td>4.50</td>
</tr>
</tbody>
</table>

The step size of the EBSD measurements was set to 0.1 μm. The specimen was mechanochemically polished with colloidal silica as an abrasive compound to obtain a smooth and damage-free specimen surface before each EBSD-measurement. The polishing depths during serial sectioning were determined by measuring the width of Vickers indents. SEM images were obtained after every sectioning and EBSD crystal orientation maps were acquired for 7 sections. The distance between subsequent layers is known within an accuracy of 0.005 μm and varies between 0.10 μm and 0.98 μm. The distances between the EBSD maps varies between 0.80 μm and 4.50 μm and are listed in Table 6-5. The seven EBSD-measurements are in total 18.0 μm apart.

The microstructures were observed in fifty sections over an area of 100×100 μm² and a total depth of 18 μm. The EBSD measurements were conducted using a field emission...
gun-equipped SEM (FEGSEM) and the TSL OIM® software for acquisition and analysis of Kikuchi patterns. Only data points with a Confidence Index (CI) higher than 0.1 were considered during analysis.

The following specific orientation relationships (OR) are taken into account in the analysis: the Kurdjumov-Sachs (K-S), Nishiyama-Wassermann (N-W), Pitsch, and (inverse) Greninger-Troiano (G-T and G-T') relationships1 [12]. The Miller-representations and the representation by the disorientation angle/axis pairs of the specific orientation relations are given in Table 6-1. The used tolerance for all orientation relationships is 2.5° around the ideal disorientation angle. With this tolerance the specific orientation relationships overlap, as the specific orientation relationships all lie close to each other around the Bain orientation relationship [12]. Therefore, when it is stated that a phase boundary has a specific orientation relationship, it is meant that one or more of the specific orientation relationships from Table 6-1 apply to the phase boundary. However, no distinction is made between the specific ORs mentioned previously in this paragraph.

6.3 Results

The two phase maps in Figure 6-1 show large FCC grains with twin boundaries and small BCC grains at grain faces, edges, or corners. The three boxes in Figure 6-1 indicate the locations of three very interesting parts of the microstructure where several nuclei appeared along the same grain boundary face. The results are presented in two main parts. In the first part an overall analysis of the seven EBSD scans is presented. In the second part the microstructures in the three boxes are studied in detail.

6.3.1 Overall analysis of the EBSD maps

Table 6-6 shows the number of BCC grains per unit grain boundary length of low-angle grain boundary (LAGBs), high-angle grain boundary (HAGBs), and twin boundary. The length of grain boundary given in Table 6-6 is the total length of grain boundary observed in the seven EBSD images per type of grain boundary (LAGB, HAGB, and twin). Table 6-6 shows that the highest nucleus density is found at high-angle grain boundaries and the lowest nucleus density is found at twin boundaries.

Figure 6-2 shows the total length of BCC/FCC phase boundary per misorientation interval of 10° as observed in the seven EBSD images per misorientation interval of 10°, including the statistical absolute error.

Table 6-6 shows the number of BCC grains per unit grain boundary length of low-angle grain boundary (LAGBs), high-angle grain boundary (HAGBs), and twin boundary. The length of grain boundary given in Table 6-6 is the total length of grain boundary observed in the seven EBSD images per type of grain boundary (LAGB, HAGB, and twin). Table 6-6 shows that the highest nucleus density is found at high-angle grain boundaries and the lowest nucleus density is found at twin boundaries.

Figure 6-2 shows the total length of BCC/FCC phase boundary per misorientation interval of 10° as observed in the seven EBSD images. Figure 6-2 clearly shows a strong maximum in the interval 40°-50°, which includes all disorientation angles of the specific orientation relationships that are listed in Table 6-1. This means that 72%, of the total phase boundary between the BCC grains and the FCC matrix grains have a specific OR. We observed this as well during an earlier study in an Fe-20Cr-15Ni alloy (mass%) [7].
Table 6-6: The number of BCC grains nucleated on FCC grain boundaries, compared by the FCC grain boundary length.

<table>
<thead>
<tr>
<th>Grain boundary</th>
<th>Length (mm)</th>
<th># BCC grains</th>
<th># grains/μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>LAGB</td>
<td>971.06</td>
<td>10</td>
<td>10.30×10⁻³</td>
</tr>
<tr>
<td>HAGB</td>
<td>4943.68</td>
<td>61</td>
<td>12.34×10⁻³</td>
</tr>
<tr>
<td>twins</td>
<td>6665.17</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

6.3.2 Detailed characterization at three different locations in the EBSD maps

Figure 6-1 shows the three different locations in the studied volume of material in which several BCC grains nucleated at the same FCC grain face. The first series of details are taken from the right-middle part of EBSD scans 1 to 5 and are shown in Figure 6-3. The region is indicated by 1 in Figure 6-1a. The second series of details are taken right from the left-top of EBSD scans 1 to 4 and are shown in Figure 6-4. The region is indicated by 2 in Figure 6-1a. The third series of details are taken from EBSD scans 6 and 7 and are shown in Figure 6-5. The region is indicated by 3 in Figure 6-1b.

In Figure 6-3 to Figure 6-5, a thick phase boundary with an asterix (*) indicates a specific orientation relation between the BCC and FCC grains. In some cases a specific orientation relationship is only present over part of the phase boundary. In these cases a BCC nucleus is considered to have an orientation relation with the FCC grain in case more than 50% of the phase boundary separating the BCC nucleus and FCC grain is characterized by a specific orientation relationship. In these cases the phase boundary is also highlighted with an asterix (*).

Location 1

Figure 6-3 shows an enlargement of the microstructure at location 1 in Figure 6-1A where several BCC grains nucleated at FCC grain boundary faces. The frames shown in Figure 6-3A are taken from EBSD scans 1 to 5 and have been labeled E1-E5, respectively. The FCC grain boundaries that are shown in Figure 6-3A are all high-angle grain boundaries. The misorientation between neighboring FCC grains is 56.2° (±0.6°) at the grain boundary face (GBF) between grain 1 and 2, 25.9° (±0.6°) at GBF 1 and 3 and 56.4° (±1.0°) at GBF 1 and 4. The GBF between FCC grain 2 and 3 and between grain 3 and 4 are twin boundaries. FCC grains 2 and 4 are separated by a twin region. The crystallographic orientation of the BCC and the FCC grains are shown in the inverse pole figures of Figure 6-3B and C, respectively.

Figure 6-3B and C also show the spread in crystallographic orientation with individual BCC and FCC grains, respectively.

Figure 6-3 shows that the BCC grains that have nucleated on GBF 1 and 2 and GBF 1 and 4 have a specific orientation relationship (OR) with both FCC grains and all these grains have the same crystallographic orientation within less than 5 degrees, which means that only one variant has nucleated at these GBFs. In case the BCC grains nucleated on the GBF 1 and 3 the BCC grains only have an OR with FCC grain 1. All BCC grains except P16 in Figure 6-3A have the same crystallographic orientation as
shown in Figure 6-3. The BCC grains P1 to P15, P17 and P18 have misorientations that do not exceed 5°, whereas the misorientation between grain P16 (dark blue) and all the other grains (red) is close to 10°. It is known that the minimum misorientation between different crystallographic variants of the BCC is 10° [15, 16], see also section 4.1. This means that two different variants have nucleated at GBF 1 and 3.

Table 6-7: Detailed information related to the microstructure shown in Figure 6-3: The average misorientation angle (including spread) between the FCC grains, the type of GBF, the number of BCC-grains having an OR with both FCC grains, one FCC grain, and having no OR with the FCC grains. In between brackets is the number of variants observed of the BCC-grains.

<table>
<thead>
<tr>
<th>FCC GBF</th>
<th>Average misorientation</th>
<th>Type GBF</th>
<th># BCC OR2 (# variants)</th>
<th># BCC OR1 (# variants)</th>
<th># BCC no OR</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-2</td>
<td>56.2±0.6</td>
<td>HAGB</td>
<td>10 (1)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1-3</td>
<td>25.9±0.6</td>
<td>HAGB</td>
<td>-</td>
<td>6 (2)</td>
<td>-</td>
</tr>
<tr>
<td>1-4</td>
<td>56.4±1.0</td>
<td>HAGB</td>
<td>2 (1)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2-3</td>
<td>59.7±0.7</td>
<td>Twin</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3-4</td>
<td>59.8±0.4</td>
<td>Twin</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 6-3 clearly shows that 12 out of 18 BCC grains (P1-4, P5-6, P8-9, P12-13 and P17-18) have an orientation relationship with both parent FCC grains and that all of these 12 BCC grains have the same crystallographic orientation, as is seen in Figure 6-3B where the crystallographic orientation of P1-4, P5-6, P8-9, P12-13 and P17-18 are indicated by the red area. It is observed that in case the BCC grains are located on the same FCC/FCC grain boundary face and have an orientation relationship with both neighboring FCC grains that only one variant of the specific orientation relationships is selected during nucleation of these BCC grains. This variant must have the lowest energy barrier for nucleation at this grain boundary face. Figure 6-3 also shows that 6 out of 18 grains (P7, P10-11, P14-16) have an orientation relationship with only one parent FCC grain and that these 6 grains do not all have the same crystallographic orientation, as is seen in Figure 6-3B where the crystallographic orientation of P7, P10-11 and P14-15 is indicated by the red area and the crystallographic orientation of P16 is indicated by the blue area. It is observed that in case the BCC grains are located on the same FCC/FCC grain boundary face and have an orientation relationship with only one FCC parent grain, that different variants are present on the same FCC grain boundary face. This has been observed before by Adachi [11] with 2D-EBSD observations. The 3D-EBSD maps used in this study show that the nuclei forming on the same FCC grain boundary with the same crystallographic orientation are not connected in the third dimension via branching see section 6.4.1.

Another difference between BCC grains P1 to P15, P17, P18 and grain P16 is that it seems that the first group grows into FCC grain 1, which is the grain that all BCC grains have an OR with, whereas P16, which has a distinctly different crystallographic orientation, seems to grow into FCC grain 3, which it does not have an OR with. This is an interesting observation for which we do not have an explanation. Detailed information related to the microstructure in Figure 6-3 is listed in Table 6-7.

Location 2

Figure 6-4 shows an enlargement of the microstructure at location 2 in Figure 6-1A where several BCC grains nucleated at FCC grain boundary faces. The frames shown in Figure 6-4A are taken from EBSD scans 1 to 4 and have been labeled E1-E4, respectively. The FCC grain boundaries that are shown in Figure 6-4A are all high-angle grain boundaries. The misorientation between neighboring FCC grains is 50.4° (±0.7°) for GBF 1 and 3, 16.5° (±0.3°) for GBF 2 and 3, 16.8° (±0.6°) at GBF 3 and 4 and to 50.3° (±0.7°) at GBF 3 and 6. The crystallographic orientation of the BCC and the FCC grains are shown in the inverse pole figures of Figure 6-4B and C, respectively. Figure 6-4B and C also show the spread in crystallographic orientation with individual BCC and FCC grains, respectively. Figure 6-4C shows that the FCC grains labeled 1, 2, 4, and 6 have approximately the same crystal orientation and could be one and the same grain with a very large orientation spread.

As observed in Figure 6-4, it clearly shows that in case the BCC grains are located on the same FCC/FCC grain boundary face and have an orientation relationship with both neighboring FCC grains that only one variant of the specific orientation relationships is selected during nucleation of these BCC grains. This variant must have the lowest energy barrier for nucleation at this grain boundary face. An example of this phenomenon is shown in Figure 6-4A on GBF 3 and 4 for P6-8 in E1 and the IPF of these BCC grains in Figure 6-4B. Figure 6-4 also shows that in case the BCC grains are located on the same FCC/FCC grain boundary face and have an orientation relationship with only one FCC parent grain, that different variants are present on the same FCC grain boundary face. An example of this phenomenon is shown in Figure 6-4A on GBF 3 and 4 for P9-10 in E3 and on GBF 3 and 4 for P13-15 in E4 and the IPF of these BCC grains in Figure 6-4B.

In addition, it is possible that on an FCC/FCC grain boundary with several BCC grains, some BCC grains have an orientation relationship with both FCC grains and some have an orientation relationship with only one FCC grain. An example of this phenomenon is shown in Figure 6-4A on GBF 2 and 3 for P3-5 in E1 where P3 has an OR with both FCC grains and P4 and P5 have an OR with only one FCC grain.
As observed in Figure 6-4C, FCC grain 4 has a very large orientation gradient. Therefore, it is possible that on the grain boundary between FCC grain 3 and 4 BCC grains with both an orientation relationship with both FCC grains as well as an orientation relationship with only one FCC grain are able to nucleate and grow into stable grains. Detailed information related to the microstructure in Figure 6-4 is listed in Table 6-8.

| Location 3 |

Figure 6-5A shows an enlargement of the microstructure at location 3 in Figure 6-1B, where several BCC grains nucleated at the same FCC grain boundary face. The frames shown in Figure 6-5A are taken from EBSD scans 6 and 7 and have been labeled E6 and E7, respectively. The misorientation between the two FCC grains in Figure 6-5A varies from 12.1° to 16.9° over the whole length of the grain boundary, which is the result of the orientation spread within the FCC grains as shown in Figure 6-5C. The average misorientation measured over 54 random points along the grain boundary is 14.3° ± 0.9°.

All BCC grains, except P6, in Figure 6-5A have an orientation relationship with both FCC grains. Sometimes the OR does not apply to the whole length of the phase boundary. We assume that during nucleation the OR applied to the whole phase boundary, but that during the inevitable growth of the grains the OR was lost due to internal strains. This assumption is based on the observation of an orientation spread within both the BCC grains and the FCC grains. The BCC grains with an OR with the parent FCC grains in Figure 6-5A all have the same average orientation and have an orientation spread within one BCC grain from 0.4° to 0.7° around the average crystallographic orientation, as can be seen in Figure 6-5B. The grain without an orientation relationship with the FCC grains has a misorientation of ~39° with neighboring BCC grains and has an orientation spread of 1.3° from the average orientation.
Figure 6-5A also shows that 3 out of 11 grains (P1-3) have an orientation relationship with only one parent FCC grain and that these 3 grains all have the same crystallographic orientation, as is seen in Figure 6-5B where the crystallographic orientation of P1-3 is indicated by the yellow area. However, BCC grains with a completely different orientation and no orientation relation with either of the two FCC grains may also nucleate, as is the case for BCC grain P6.

This indicates that the activation energy for nucleation is lower in case the BCC-grain has an OR with both FCC grains than in case the BCC-grain has an OR with one FCC grain, which in turn has a lower activation energy for nucleation than the BCC-grain that has no OR with the FCC grains. Detailed information related to the microstructure in Figure 6-5 is listed in Table 6-9.

Table 6-9: Detailed information related to the microstructure shown in Figure 6-5: The average misorientation angle (including spread) between the FCC grains, the type of GBF, the number of BCC-grains having an OR with both FCC grains, one FCC grain, and having no OR with the FCC grains. In between brackets is the number of variants observed of the BCC-grains.

<table>
<thead>
<tr>
<th>FCC GBF</th>
<th>Average misorientation</th>
<th>Type GBF</th>
<th># BCC OR2 (# variants)</th>
<th># BCC OR1 (# variants)</th>
<th># BCC no OR</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-2</td>
<td>14.3±0.9</td>
<td>HAGB</td>
<td>7 (1)</td>
<td>3 (1)</td>
<td>1</td>
</tr>
</tbody>
</table>

6.4 Discussion

6.4.1 Multiple nuclei versus a single nucleus

As observed in earlier studies, it is shown that specific orientation relationships play an important role during nucleation of BCC grains in an FCC matrix [7, 17]. When several BCC grains nucleate on the same GBF with approximately the same orientation, e.g. as observed in Figure 6-3, the question arises what caused this phenomenon. There are two explanations, the first being that the BCC grains are not individual grains, but are the branches of a BCC grain that extends along the whole of the GBF. Proof of this should be found in the observation of a large BCC grain that connects all branches in another section similar to what is observed recently in a 3D-study of the precipitation of the α-phase in a β-phase matrix in titanium alloys [18, 19]. We have not observed such a large BCC grain in the EBSD scans or the additional SEM pictures. However, because of the limited accuracy of aligning the EBSD images, we need an additional criterion. We have looked at the spread within one individual grain, which is around 0.5°, and...
the misorientation between two different grains, which is larger than the spread around 2-3° or higher.

In order to establish that the BCC grains in the EBSD scans are part of one and the same grain the orientation spread of the individual grains and the misorientation between the grains in one EBSD scan and the subsequent EBSD scan are compared. This is done for EBSD scans 1 to 3 for location 1 (Figure 6-3) and location 2 (Figure 6-4). The other EBSD scans are far apart that it does not seem likely that the BCC grains are connected over these distances.

For the BCC grains at location 1, it is observed that the orientation spread in each individual BCC grain is between 0.4°-0.8° as is listed in Table A-1 of the Appendix. In addition, the misorientations between the BCC grains in subsequent EBSD scans are of the order of a few degrees and are listed in Table A-3 of the Appendix.

For the BCC grains at location 2, it is observed that the orientation spread in each individual BCC grain is between 0.3°-0.8° and are listed in Table A-5 of the Appendix. In addition, the misorientations between the BCC grains in subsequent EBSD scans are of the order of tens of degrees and are listed in Table A-7 of the Appendix.

From the above it can be concluded that the observed BCC grains are all individual grains that originate from individual nuclei.

The second explanation can be found in local variant selection, see next subsection. In this case only one variant out of 72 (24 K-S, 12 N-W, 12 Pittsch, 12 Greninger-Troiano and 12 inverse Greninger-Troiano) results in a minimal energy barrier for nucleation. Local variant selection would be strongly promoted in case nuclei would form with a geometry corresponding to the coherent pillbox model. This model assumes that the BCC grains have coherent phase boundaries that are parallel to the parent FCC grain boundary. From this assumption, it can be gathered that coherent pillbox shaped nuclei nucleate at twin boundaries or low angle grain boundaries between the FCC grains, because only at twin boundaries and very LAGB it would be possible to form coherent interfaces with both FCC grains. Interestingly, most of the BCC grains that we observe did NOT nucleate at twin boundaries or low angle grain boundaries, see section 5.3 of Chapter 5.

It is observed that none of the BCC grains have nucleated on FCC twin boundaries. However, the length of the FCC twin boundaries is greater than that of the FCC high-angle grain boundaries and the FCC low-angle grain boundaries. Relatively speaking, the FCC twin boundaries are then even less preferred for nucleation. For comparison the number of BCC grains per FCC grain boundary species and the length of each FCC grain boundary species are listed in Table 6-62.

6.4.2 Variant selection

In the studied details from Figure 6-3, Figure 6-4 and Figure 6-5 it is observed that in case the BCC grains that are formed on the same FCC/FCC GBF have an orientation relationship with both FCC grains then the difference in crystallographic orientations between these BCC nuclei is smaller than 5°. This means that only one variant of the crystallographic orientation relationships has been selected for these grains, since the misorientation between these grains (< 5°) is less than the minimal misorientation between two BCC variants nucleated from the same FCC grain.

In Figure 6-4 it is observed that when BCC grains are located on the same FCC/FCC grain boundary and have an orientation relationship with only one neighboring FCC grain, they do not necessarily have the same crystallographic orientation. The misorientations between these grains are larger than 10°. Considering the misorientation angles between variants of the KS and NW OR, it can be seen from Figure 6-4 that several variants of the specific orientation relationships are selected for these BCC grains. This probably means that different variants can lead to a similar low energy barrier for nucleation at this grain boundary face. These observations were also made by Adachi et al. [11] for variants of the KS orientation relationship in a Ni-43Cr (mass%) alloy.

The present observations show a strong variant selection mechanism has been active which only selects several variants out of a range of 72 possible ones. As it is obvious that nucleation is driven by minimization of the Gibbs free energy one should consider the orientation dependent terms in the energy balance in order to explain the variant selection mechanism. One such orientation dependent component is the elastic energy term, which is crystallographically anisotropic for FCC and BCC crystal structures and hence will affect the energy balance for different crystallographic variants of the product phase [20-23].

2 Note: We did not calculate the nucleus density of BCC grains on FCC grain boundary faces from a 3D reconstruction of the microstructure. Instead, we calculated the total length of FCC/FCC grain boundaries as observed in the EBSD images.
6.4.3 Nucleation mechanism

In earlier research \[4\] it was found that a pillbox shaped nucleus with coherent phase boundaries and specific orientation relationships between the FCC and BCC phase could explain the high nucleation rates. All phase boundaries involved are (semi-) coherent and represent a specific orientation relationship. The shape of the nucleus then requires that this nucleus can only originate at coherent grain boundary faces. However, these requirements lead to the assumption that nucleation could only take place at special grain boundary faces, e.g. coherent twin boundaries and very low-angle grain boundaries.

From the details shown in Figure 6-3, Figure 6-4 and Figure 6-5 it is observed that nucleation of BCC grains takes place on random (incoherent) high-angle grain boundaries and that specific orientation relationships still play a large role in this process. It is thus that a specific orientation relationship between two neighboring parent grains and a product grain does not automatically imply that the two parent grains share a coherent grain boundary face, as coherency depends on both the misorientation as well as the inclination of the grain boundary face. In case a BCC nucleus can nucleate on a grain boundary face such that it can obtain a specific orientation relationship with the two neighboring FCC grains, the geometry of the nucleus is determined by the formation of a coherent grain face in each of the two neighboring FCC grains. As a result, the BCC/FCC phase boundaries with a specific orientation relationship can still be coherent, but the requirement that the FCC/FCC grain boundary face where the nucleus originates must be coherent is made redundant.

In general, it is assumed that both phase boundaries do not need to be parallel to each other or to the FCC/FCC interface. The coherent BCC/FCC interfaces are formed by parallel \{110\}-planes of BCC and \{111\}-planes in FCC, as is the case for the abovementioned orientation relationships. Since the two sets of \{111\}-planes in the two FCC-grains will in general not be parallel, two different sets of \{110\}-planes of the BCC-grain will be involved. The two coherent BCC/FCC interfaces of the nucleus will therefore not be parallel, but make angles that are equal to the angles between the six different orientations for \{110\}-planes in a single grain.

The conditions for the nucleus geometry stated above have the consequence that only some variants of the orientation relationships apply for the given parent grain orientations, as is observed in this experiment and has been discussed in the previous section. Variant selection has been observed in earlier research as well \[11, 24, 25\].

It must be pointed out that nucleation is a statistical process, which means that under the same circumstances, a less preferred and favored nucleus, i.e. with phase boundaries that do not have the lowest possible interphase energy, can nucleate. Therefore, it is possible that on the same FCC grain boundary both BCC grains with two phase boundaries with a specific orientation relationship and BCC grains with one phase boundary with a specific orientation relationship are observed.

In general, it seems that these observations imply that the barrier for nucleation for a BCC nucleus with an OR with both parent FCC grains is lower than the barrier for nucleation for a BCC nucleus with an OR with one parent FCC grain, which in turn is lower than the barrier for nucleation for a BCC nucleus with no OR with the parent FCC grains: \(\Delta G^*(OR2) < \Delta G^*(OR1) < \Delta G^*(no OR)\). For a BCC grain to have two phase boundaries with a specific orientation relationship, it is necessary to have an FCC grain boundary with a specific relationship between the two neighboring FCC grains. Twin boundaries are an example of such a specific relationship between two FCC grains. In addition, a specific relationship between two FCC grains exists when the misorientation between the FCC grains is similar to one of the misorientations between two variants of a specific BCC/FCC orientation relationship \[15, 16\], as described in the previous section.

The average misorientation angles between the FCC grains and the number of specific orientation relationships of the BCC grain nucleated on that FCC/FCC grain boundary as shown in Figure 6-3, Figure 6-4 and Figure 6-5, are listed in Table 6-7, Table 6-8 and Table 6-9, respectively. It is observed that when BCC grains have nucleated with a specific orientation relationship with both FCC parent grains, the FCC/FCC misorientation angle (including the uncertainty defined by the spread) coincides with one of the misorientation angles between two variants of variants according to one of the orientation relationships listed in Table 6-1 to Table 6-3.

6.4.4 Geometry of the nucleus

The nucleus geometries like the spherical cap models and the pillbox models as described in Chapter 2 do not seem to be applicable to the observations from the experimental results. The spherical cap models do not include the specific orientation relationships between the parent and the product phase, i.e. the FCC and the BCC phase, that obviously had a large influence on the nucleation of the product phase. In addition, the pillbox models do not explain the large number of BCC grains that have nucleated on what seem to be random high angle FCC/FCC grain boundaries. The coherent pillbox model requires that the BCC grain has an OR with both FCC parent grains and...
that the phase boundaries are all coherent or semi-coherent. However, the coherency of a phase boundary is not related to the phase boundary having an OR. In addition, this coherency requirement implies that the grain boundary between the FCC parent grains should be coherent. This is the case for twin boundaries. It should be pointed out that coherent interfaces are very stable and have a low interface energy. The energy barrier for nucleation at these kind of interfaces is relatively high and therefore not preferred. It is observed that the BCC grain density is lowest at twin boundaries, according to Table 6-6.

In order to obtain a specific orientation relationship between the FCC and BCC phase, the (111)-planes of the FCC phase and the (110)-planes of the BCC phase have to be parallel, see Table 6-1. It is known that for every grain boundary the grain boundary geometry can change along the dimensions of the grain boundary. As a consequence, the geometry of a nucleus will be different for every parent grain boundary it has nucleated on. In addition, the nucleus will not have the same geometry at each location on a grain boundary.

An example of a nucleus geometry, it is proposed that the pillbox-shaped BCC nucleus should not be parallel to the FCC/FCC grain boundary, but that the FCC/FCC grain boundary is inclined and is intersected by the BCC nucleus. With this new pillbox model the presence of specific orientation relationships at the phase boundaries is explained and, additionally, the number of possible FCC/FCC grain boundaries suitable for such nucleation is increased with the number of possible misorientations between the variants of the specific orientation relationships between BCC and FCC. The new pillbox model is shown in Figure 6-6 where the (111)-planes of the FCC phase and the (110)-planes of the BCC nucleus are indicated.

![Figure 6-6: Proposed new pillbox model with the BCC nucleus inclined and intersecting at the FCC/FCC grain boundary face. The phase boundaries are either coherent or semi-coherent, according to the traditional coherent pillbox model. The solid and dashed lines in the BCC nucleus and the FCC grains represent [110]-planes and [111]-planes, respectively.](image)

6.5 Conclusions

1. a. The EBSD maps show that 53% of the total length of FCC/FCC grain boundary is a twin boundary, and less than 10% of the BCC-grains nucleated on a twin boundary. This is much less as would be expected from the coherent pillbox model.

b. More than 70% of the total length of phase boundary between the BCC grains and the neighboring FCC matrix grains is characterized by a specific orientation relationship between the BCC and FCC phases.

2. Three types of BCC nuclei have been found: BCC nuclei without a specific orientation relationship with any of the two neighboring FCC grains, BCC nuclei with a specific orientation relationship with only one of the two neighboring FCC grains, and BCC nuclei with a specific orientation relationship with both neighboring FCC grains.

3. In case the BCC grains are located on the same FCC/FCC grain boundary face and have an orientation relationship with both neighboring FCC grains, it is found that these BCC grains have the same crystallographic orientation within 5°. This small angular deviation means that only one variant of the specific orientation relationships is selected during nucleation of these BCC grains, which is the variant with the lowest energy barrier for nucleation at this grain boundary face.

4. All the BCC-nuclei having a specific orientation relationship with both neighboring FCC-grains form on incoherent high-energy FCC/FCC grain boundaries. This does not correspond to the coherent pillbox model. A modified pillbox model is presented.

5. The FCC/FCC grain boundary faces that have BCC nuclei with a specific orientation relationship with any of the two neighboring FCC grains, have a specific misorientation angle, corresponding with the misorientation angles between the variants of the specific orientation relationships.

6. The 3D-EBSD maps show that multiple nuclei form on the same FCC grain boundary with the same crystallographic orientation. The nuclei are not connected in the third dimension and as such these nuclei do not originate from one nucleation event plus subsequent growth in a branched manner. Instead,
these nuclei have formed during individual nucleation events.

7. In case the BCC grains are located on the same FCC/FCC grain boundary face and have an orientation relationship with only one FCC parent grain, it is found that different variants are present on the same FCC grain boundary face.

8. Even if it is possible to form nuclei with coherent interfaces with both FCC-grains, nuclei may still form on the same FCC/FCC grain boundary face without having a specific orientation relationship with either of the two FCC-grains.

9. In case a BCC-grain is present on an FCC/FCC GBF having an orientation relationship with both parent grains, the majority of the nuclei on that GBF will nucleate according to this variant.

10. There seems to be the following trend: The number of BCC-grains with an OR both FCC-grains is higher than the number of BCC-grains with an OR one FCC-grain, which is higher than the number of BCC-grains without an OR with the FCC grains.

6.6 Acknowledgements

This chapter could not have been written without data of Mr. T. Takeuchi, graduate student, and Prof. Dr. M. Enomoto of Ibaraki University and Dr. Y. Adachi, NIMS, Japan. The additional explanation of Dr. Y. Adachi is greatly appreciated. I wish to thank Prof. Dr. ir. J. Sietsma for carefully reading and discussing this chapter.

6.7 References


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Towards 3D-reconstruction of the austenitic microstructure from 3DXRD-diffraction patterns
7. Towards 3D-reconstruction of the austenitic microstructure from 3DXRD-diffraction patterns

7.1 Introduction

For a long time steel has been and is still being used more than other metals, because of good physical, thermal, and mechanical properties and low costs. For this reason steel has been investigated intensively in order to get a better understanding of the metallurgical mechanisms during the production processes. Understanding the metallurgical process is important for the development of new steel grades with optimal properties and for improving existing steel grades. The properties of steel depend critically on the microstructure, which is formed during the production process. Grain nucleation and grain growth are two processes that play a crucial role in the evolution of the microstructure. Despite the various models that have been developed and the experimental efforts that have been made in the last 60 years, the underlying mechanisms of the phase transformation processes are still not fully understood.

Recently, Three Dimensional X-Ray Diffraction (3DXRD) was developed to study the behavior of grains in the bulk of the material [1-7]. 3DXRD is a non-destructive method that can give in-situ information about the fractions of the phases present and the nucleation and growth of the individual grains during phase transformations [5]. The microstructure of bulk crystalline materials can be characterized in terms of the crystal orientation, position, and shape of the boundary of the grains in the specimen. The technique uses high-energy X-rays from a synchrotron source and generates diffraction patterns of bulk-size samples, i.e. in the order of millimeters instead of micrometers as is common for laboratory X-ray diffraction equipment.

The microstructure of aluminum has been reconstructed in three dimensions from the X-ray diffraction patterns by using specially developed reconstruction algorithms [6-8]. It was shown that in case time-dependent 3DXRD-scans are performed during recrystallization, a four-dimensional reconstruction of the growth of an individual grain can be made.

In this chapter, a method is developed and a first attempt is made to reconstruct the 3D structure of the austenite phase from 3DXRD-data, which was measured on a high-purity Fe-Cr-Ni alloy at room temperature. One of the differences between aluminum and austenite is that the austenite microstructure contains many twin-related grains. This results in spot overlap in the diffraction patterns, which makes the data-analysis more complex. In order to investigate this in more detail the diffraction of two twin-related austenite grains is simulated and 3DXRD experiments have been performed on an austenitic microstructure containing annealing twins.

7.2 Simulation of 3DXRD diffraction patterns of two twin-related FCC grains

A twin consists of two FCC grains that have a special crystallographic orientation relationship with each other, which can be described by a rotation of 60° around the <111> axis of one of the two FCC grains. This <111>/60° orientation relationship can give rise to complications during the 3DXRD data-analysis, because some of the diffraction spots of the two twin-related FCC grains might overlap. The diffraction patterns of two twin-related grains are simulated in order to find out how this orientation relation affects the 3DXRD diffraction patterns.

The simulations have been performed with the software PolyXSim, which is developed by H.O. Sørensen of the Risø National Laboratory, Technical University of Denmark, Denmark [9]. PolyXSim is a program that simulates 3DXRD diffraction patterns of polycrystalline (multiphase) materials for the “far-field” case in mode 2, see also Chapter 4. This means that the detector is placed at such a distance from the specimen that the position of the spots on the detector is mainly determined by the orientation of the crystal lattices that are in reflection. This is contrary to the 'near-field' case in mode 2, see also Chapter 4, in which the position of the spots on the detector is determined by the crystallographic orientation and the position of the grain in the specimen.

The following assumptions are made in PolyXSim: 1) the X-ray beam is mono-chromatic with no divergence and energy spread, 2) the data acquisition takes place while rotating the sample around the \(\omega\)-axis (see chapter 4) in equidistant steps, 3) the detector is perpendicular or tilted relative to the beam and has a fixed distance to the centre of rotation, and 4) a detector is used that accounts for spatial distortion, the point-spread function, and the flood field.

The 3DXRD-diffraction patterns of an FCC-grain are calculated for a rotation of the crystal over 360 degrees around the \(\omega\)-axis. The \(\omega\)-axis is perpendicular to the incoming beam. The orientation of the single crystal with respect to the \(\omega\)-axis and the incoming beam is such that all planes of the following families of planes come into reflection during rotation over 360 degrees: \{111\}, \{200\}, \{220\}, \{311\}, and \{222\}. The number of spots on the detector that are related to a certain set of lattice planes is equal to the
multiplicity of that set of lattice planes times two. The factor two arises, because of the cubic symmetry of the FCC-crystal. The total number of spots for each family of planes is listed in Table 7-1: Number of diffraction of spots of a single crystal rotated over 360° and the number of overlapping spots for each diffraction ring. For the situation in which the single crystal is rotated over 360°.

<table>
<thead>
<tr>
<th>Diffraction ring</th>
<th>Plane</th>
<th># Spots grain 1</th>
<th># Spots grain 2</th>
<th># Overlapping spots</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>111</td>
<td>16</td>
<td>16</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>200</td>
<td>12</td>
<td>12</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>220</td>
<td>24</td>
<td>24</td>
<td>12</td>
</tr>
<tr>
<td>4</td>
<td>311</td>
<td>48</td>
<td>48</td>
<td>24</td>
</tr>
<tr>
<td>5</td>
<td>222</td>
<td>16</td>
<td>16</td>
<td>4</td>
</tr>
<tr>
<td>Total:</td>
<td></td>
<td>116</td>
<td>116</td>
<td>44</td>
</tr>
</tbody>
</table>

A second simulation is performed for the twin-related grain. Both grains are treated as single crystals, but the orientation of the first single crystal has a twin orientation relationship with the second single crystal. The diffraction patterns of both grains are shown in Figure 7-1 after rotation over 360° while continuously exposing the grain to the synchrotron beam. The diffraction pattern in Figure 7-1A contains less spots than in Figure 7-1B. The reason for this is that in Figure 7-1A a number of spots appear at the same (θ,η)-location, due to the specific orientation of the first grain with respect to the rotation axis and the direction of the X-ray beam. These spots appear at different ω-locations, and can thus be distinguished from each other. However, this cannot be seen in 'integrated' image of Figure 7-1A, in which all diffraction patterns that are generated during rotation over 360°, are added up.

It is observed that all rings except ring 2, which is related to the {200}-planes, have overlapping spots. The maximum overlap is 50% for the {220}- and the {311}-planes.
The material is homogenized at 1200°C for 10 hours and then quenched to room temperature. Subsequently, the material is machined with the dimensions shown in Figure 7-3. The exact location of beam with respect to the specimen can be determined by scanning the specimen in a vertical direction with the beam. At the bottom of the specimen the diameter changes leading to a change in intensity of the primary beam. At the top of the specimen the density of the illuminated material changes leading to a change in intensity of the primary beam.

The incoming beam penetrates through the sample and as soon as the Bragg conditions are fulfilled the X-rays will be diffracted. A typical diffraction pattern of the Fe-20Cr-10Ni alloy is shown in Figure 7-5. A ring consists of a number of individual spots, each representing an individual grain in case there is not spot overlap, all diffracted under the same Bragg angle. The integrated intensity of a spot is directly proportional to the volume of the grain. It must be noted that the integrated intensity of a spot can be distributed over multiple images [11].

**Figure 7-4:** Schematic drawing of the experimental set-up for the 3DXRD measurements. The set-up consists of dual Laue crystals, slits and a 2D detector. The specimen is positioned on a table that can be translated and rotated [Hemant Sharma].

**Figure 7-5:** X-ray diffraction pattern of the Fe-Cr-Ni alloy showing the austenite rings.

### 7.3.2 3DXRD microscope

A monochromatic X-ray beam with energy of 71.68keV was obtained with two bent Laue crystals. The beam size was 1200*400µm² (width x height). The beam is wider (1.20 mm) than the diameter of the sample (1.0 mm). The specimen was positioned in such a way that the width of the specimen remained inside the beam during rotation. The specimen was illuminated 2 mm below the top of the specimen. The sample was rotated in steps of Δω=0.5° over an angle of 200° around an axis perpendicular to the beam with an exposure time of 0.35s per 0.5°. The diffracted beams were collected on a two-dimensional FReLoN2K CCD camera detector with an area of 2048*2048 pixels and an effective pixel size of approximately 50 µm. The average dark current (electronic noise) of the FReLoN2K detector is 1000 cts/pixel. The maximum intensity is 65'000 cts/pixel. The detector was placed at different positions of approximately 225, 240, and 255 mm from the sample [10]. The sample is installed on a high-precision, air-bearing rotation table that is used for rotating the specimen over an angle ω and on a translation table for translating in the (x,y,z) direction, see Figure 7-4. Ideally, the direction of the synchrotron beam and the rotation axis would be perpendicular. The wedge is the angular deviation from this orthogonality. In this experiment the wedge was negligibly small.

The incoming beam penetrates through the sample and as soon as the Bragg conditions are fulfilled the X-rays will be diffracted. A typical diffraction pattern of the Fe-20Cr-10Ni alloy is shown in Figure 7-5. A ring consists of a number of individual spots, each representing an individual grain in case there is not spot overlap, all diffracted under the same Bragg angle. The integrated intensity of a spot is directly proportional to the volume of the grain. It must be noted that the integrated intensity of a spot can be distributed over multiple images [11].
7.4 Data-analysis method

The 3D-microstructure is reconstructed from the 360 diffraction patterns that were recorded during rotation over the first 180° (the data during rotation from 180-200° was not used). The data-analysis consists of a number of steps:

1. Pre-processing
2. Determination of the crystal orientation
3. Determination of the grain volume
4. Determination of the position of the grain in the specimen.

These steps in the data-analysis are not executed independently from each other, except for the pre-processing step, as will become clear in the following. The data-analysis is performed with the Fable software [12] and additional software developed in Delft as will be explained in the following sections. Fable is a software package that is developed by the staff at beam line ID11 at the ESRF in France and the Risø National Laboratory, Technical University of Denmark, Denmark.

7.4.1 Pre-processing

The pre-processing of the diffraction images consists of three main components:

1. Corrections for the non-ideal response of the detector: a) flood field correction, b) spatial distortion correction, and c) dark current subtraction.
2. Calibration of the geometrical parameters of the experimental set-up: a) detector tilt, b) sample-to-detector distance, and c) beam center.
3. Characterization of the position of the diffraction peaks.

Firstly, the flood field correction is made to correct for differences in response of pixels to a uniform illumination of the detector. Subsequently, the dark current, which is the electronic noise of the detector, is subtracted.

Secondly, the position of the diffraction peaks on the detector is determined. In the diffraction patterns the intensities of all diffracted peaks as well as noise are recorded. The diffraction peaks can be found by using a threshold intensity. Pixels with intensity below this threshold are discarded. Choosing the right threshold intensity is important, because this will influence the final result of the 3D-reconstruction. When the threshold is too low, spurious spots not belonging to any grain will be found. In addition, in case the threshold is too low the diffraction spots start to overlap, leading to missing peaks during indexing and incorrect peak position. A too high threshold means that weak diffraction peaks from smaller grains will be missed. The threshold used in this data processing is 500 cts/pixel above the dark current.

Thirdly, the spatial distortion correction is applied to the positions of the diffraction peaks.

Fourthly, the geometrical parameters of the experimental set-up are determined, which requires the lattice parameter and crystal structure of the specimen to be known. The relationship between the austenite composition of Fe-20Cr-12Ni and the lattice parameter at room temperature (300K) can be described as follows [13]:

\[
a_{\text{Fe}}^{\text{a}} = a_{\text{Fe}}^{0} - 0.0002x_{\text{Fe}} + 0.0006x_{\text{Cr}}.
\]

where \(a_{\text{Fe}}^{0}\) is the lattice parameter of pure iron in the austenite phase in nm at room temperature and \(x_{i}\) represents the mole fraction of element \(i\) in the austenite phase in at.%. With \(a_{\text{Fe}}^{0} = 0.35780\) nm for pure iron at 300K, the lattice parameter for the austenite phase \(a_{\text{Fe}}^{\text{a}}\) in Fe-20Cr-12Ni is 0.35876 nm. Some crystallographic and scattering information for both the austenite and the ferrite phase is given in Table 7-2.

<table>
<thead>
<tr>
<th>Crystal structure</th>
<th>Crystallographic plane</th>
<th>(a) (nm)</th>
<th>(h^2+k^2+l^2)</th>
<th>(2\theta) (°)</th>
<th>(d) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FCC (200)</td>
<td>0.35876</td>
<td>4</td>
<td>2.77235</td>
<td>5.5447</td>
<td>0.17938</td>
</tr>
<tr>
<td>BCC (200)</td>
<td>0.28848</td>
<td>4</td>
<td>3.44846</td>
<td>6.89692</td>
<td>0.14424</td>
</tr>
<tr>
<td>FCC (220)</td>
<td>0.35876</td>
<td>8</td>
<td>3.92222</td>
<td>7.84444</td>
<td>0.12684</td>
</tr>
<tr>
<td>BCC (211)</td>
<td>0.28848</td>
<td>6</td>
<td>4.22479</td>
<td>8.44958</td>
<td>0.11777</td>
</tr>
</tbody>
</table>
Fifthly, the position of the diffraction peaks can now be expressed in terms of \((\theta, \eta, \omega)\)-coordinates, which can be translated into the G-vectors corresponding to the diffraction spots, see Chapter 4.

Table 7-3: Fitted parameters for the indexing of diffraction spots for the 3DXRD sample.

<table>
<thead>
<tr>
<th>Sample-detector distance (mm)</th>
<th>Fitted distance (mm)</th>
<th>Beam center Y (pix)</th>
<th>Beam center Z (pix)</th>
<th>Tilt Y (rad)</th>
<th>Tilt Z (rad)</th>
</tr>
</thead>
<tbody>
<tr>
<td>225</td>
<td>222.77</td>
<td>1078.16</td>
<td>1018.85</td>
<td>-0.01</td>
<td>-0.0296</td>
</tr>
<tr>
<td>240</td>
<td>237.53</td>
<td>1070.52</td>
<td>1018.82</td>
<td>-9.59*10^{-3}</td>
<td>-0.0288</td>
</tr>
<tr>
<td>255</td>
<td>252.24</td>
<td>1062.30</td>
<td>1018.66</td>
<td>-9.31*10^{-3}</td>
<td>-0.0295</td>
</tr>
</tbody>
</table>

The diffraction spots in all images acquired during rotation over 180° are summed up in one image to determine the geometrical parameters of the set-up, see Figure 7-6. In Figure 7-7 the ‘unfolded’ diffraction pattern from Figure 7-6A is shown, wherein the \(\eta\)-angle is plotted as a function of the 2\(\theta\)-angle. The small pink lines, indicated by circles, show the 2\(\theta\)-angles of the centre of the diffraction rings. The detector tilt, sample-to-detector distance, and beam center are fitted to the experimental data, using the information on the crystal structure and lattice parameter as input. The wavelength is also given as an input. The fit-parameters are given in Table 7-3.
The (200)-plane of an arbitrary oriented FCC-grain will be reflected 6 times on average during rotation of the specimen over 180°. However, some orientations will result in only four spots, for example, when the <100> crystal axes are parallel to the direction of the beam. The spots need to be grouped or indexed according to the grain to which they belong. Subsequently, the orientation and position of the grain in the specimen can be calculated. The position of a spot on the detector is determined by the orientation and position of the grain in the specimen, which is illustrated in Figure 7-8. Consider the situation in which three grains, indicated A, B, and C in Figure 7-8, have the same crystallographic orientation. The position of the three spots on the detector is different for the three grains due to the slightly different positions of the grains in the specimen. This information is used to calculate the position of the grain in the specimen. However, this is not straightforward, because two grains with slightly different orientations and different positions in the specimen could lead to a spot at the same position on the detector. This is illustrated by grains C and E in Figure 7-8. Grains D and E have the same crystal orientation, which is different from the orientation of grains A, B and C.

The approach is to calculate the theoretical positions of the spots for a grain that is located at the center of the illuminated volume. This is done for all possible orientations by stepping through the orientation space with discrete steps. This procedure results in a list of spot positions for a set of grains with different orientations (covering the entire orientation space). All these grains are assumed to be located at the center of the illuminated volume.

A list of spot positions is also obtained from the experiment. The (θ, η, ω)-coordinates of a spot are determined from the experimental data by assuming that the beam center for a grain is the same as the beam center of the average of the grain ensemble. This is the beam center as determined in the previous section. However, for each individual grain the ‘beam center’ is slightly different than the average of the grain ensemble. The ‘beam center’ of an individual grain should be the projected position of the grain on the detector along the direction of the primary beam. The ‘beam center’ of a grain changes during rotation of the specimen, in case the grain is not located along the axis of rotation of the set-up. In other words, for each spot of a grain a different beam center needs to be determined in order to calculate the (θ, η)-coordinates of the spot. However, this is initially not possible, because the grain position is not known a priori. Initially, the (θ, η)-coordinates of the spot are calculated from the beam center of the average of the grain ensemble.

The experimental and theoretical spot positions are compared to find matches. However, a search range needs to be applied to be able to compare the theoretical and experimental spot positions, due to the experimental uncertainty in determining the spot positions of a grain and the position of the grain in the specimen, which is not known a priori, has a significant effect on the position of the spot on the detector. The range in which to look for spots from the experiment is indicated by a (Δθ, Δη, Δω)-range around the theoretical spot position. Indexing of the spots depends highly on the search range that is chosen. The main problem that may arise during indexing is that two or more spots from different grains can be located so close to each other that they fall within the search margins, resulting in spots being wrongly assigned to grains. In case the range is set too narrow too few grains will be indexed. For the processing of the experimental data the search range is indicated in Table 7-4.

Table 7-4: List of input parameters used for the indexing of the diffraction spots.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Δθ (°)</th>
<th>Δη (°)</th>
<th>Δω (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value (2σ)</td>
<td>0.2</td>
<td>0.6</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Figure 7-9: A) Example of an indexed grain with a large discrepancy in grain diameters and internal angles, which is a measure of the error in the indexing. The non-matching spots are discarded; B) Example of an indexed grain with a discrepancy in internal angles, but matching grain diameters. The non-matching spots are discarded; C) Example of an indexed grain with a discrepancy in grain diameters, but matching internal angles. The non-matching spots are discarded; D) Example of an indexed grain with grain diameter differences less than 5 µm and internal angles smaller than 0.05°, and at least four spots. All spots are indexed as one and the same grain.
For the moment, we assume that the spots are assigned correctly to grains, although it is quite likely that some spots have been assigned incorrectly to grains. The orientation of the grain is approximately known by grouping the spots. The center of mass of the grain can then be calculated in the following way. The 20-coordinate of a spot on the detector as calculated from the beam center of the grain ensemble, is slightly different than the average 20-coordinate of the total grain ensemble, because the grains are not all located in the center of the illuminated volume. This shift in spot position on the detector expressed in micrometers is directly related to the distance from the rotation axis to the position of the grain in the specimen. As a first step, the orientation of the grain is fixed. Theoretical spot positions are now calculated for the situation in which the grain position is changed in the specimen. A best fit with the 6 spots of one grain is found. Thus, an approximate grain position is obtained. In an iterative process the grain orientation and the grain position are changed slightly in an alternating manner to find the best fit for the orientation and grain position.

The remaining problem is that some spots have been assigned wrongly to a grain. In order to check this we have implemented two criteria. Therefore the ‘internal angle (IA)’ of each spot is determined, which is a measure of the error in indexing. The internal angle is the angle between the theoretical and the measured G-vector in reciprocal space. The internal angle should be low, <0.05 is a good value. In addition, the indexing results are filtered by accepting only indexed grains with at least four spots and that have a grain diameter that is not too different (5 μm in diameter) from the average grain diameter as calculated from the set of spots:

\[
|\text{grain diameter} - \text{average grain diameter}| < 5 \mu\text{m} \quad \text{AND} \quad \text{IA} < 0.05
\]  

7-2

Figure 7-10: Number of well-indexed grains per indexing iteration step. The number of spots used per iteration step is the total number of spots minus the spots of the previously well-indexed grains.

Without this filtering, it is possible that the spots used for the indexation of one grain, show a large difference in grain size. This can be explained by Figure 7-9. In Figure 7-9A the calculated volume and the internal angle (IA) per spot are shown. It is observed that four out of six spots (2, 3, 4, 5) represent grains with approximately the same grain radii and small internal angles. It is assumed that spots 2, 3, 4, 5 represent the same grain. However, spots 1 and 6 represent grains with much larger grain radii and large internal angles, i.e. a large error in indexing. It is assumed that spots 1 and 6 do not represent the same grain as spots 2, 3, 4, 5. Therefore, spots 1 and 6 are discarded.

Figure 7-11: 3D diagram of the cloud of centers of mass of the indexed grains. A) Isometric view; B) Top view, showing the circular area of the irradiated cylinder shaped volume of the sample. The circle indicates the shape of the cylinder.
7.4.3 Ray-tracking

An alternative method to find the position of the grain in the sample is to use the three detector distances for ray tracking [8, 14]. In theory, for each spot found on the detector at the first detector distance one should find a spot on the detector at the second and the third detector distance. Since the number of spots decreases for larger distances, due to the divergence of the diffracted beam, some spots found on the detector at the first detector distance will not be found at the second or third detector distance. This is mainly the case for the outer rings of the {311}- and {220}-planes.

To find corresponding spots on the detector at the 3 different detector distances a spot found at distance 1 and a spot found at detector 2 that have values for 2θ, η and ω close to each other, are considered to come from the same grain. In other words: when the difference between the values for 2θ is smaller than 0.1, for η smaller than 1 and for ω smaller than or equal to 0.5, the spots are considered to come from the same grain. These values are relatively small; therefore when two spots are nearly coinciding on the detector, they both fulfill this rule.

Another approach in this tracking method is to compare the vector from the center of the sample to the spot on the detector at the first distance and the second distance. If those vectors lie closely together, the spots can be regarded as coming from the same grain. The disadvantage of this approach is that most grains are not right in the center of the sample, which causes a deviation in the vectors. The angle between the two vectors must be smaller than a pre-set maximum value, usually 0.08°. If more than one spot is a candidate, the spot with the smallest difference in the vectors is chosen.

A total of 13'000 spots were found on the detector at the first detector distance. For 500 spots found at the first detector distance there was no corresponding spot found on the detector at the second detector distance. For 1000 spots found at the first detector
distance there was no corresponding spot found on the detector at the third detector distance.

Finally a line is fitted through the spots on the detector at the three detector distances and traced back to the sample. This is done for all spots within the ω-rotation range coming from the same grain. Ideally this would form an intersection point at a certain position in the sample, which would then be the center of mass of the grain.

However, in practice the ‘rays’ do not intersect in one point. In Figure 7-14 an example of a relatively good and a relatively bad fit are shown. The figure shows the diffraction vectors for one grain in different views: overview, side view zoomed in, top view zoomed in. In both examples the ‘rays’ traced from the spots on the detector at the three distances do not intersect at one center of mass, but form a cloud of intersection points. In the relatively good fit, the cloud is denser than for the relatively bad fit.

A reason that the intersection points form a cloud is that the ray tracing method is very sensitive to small errors in the location of the spots. If the position of the spot on the detector at the third distance is off by 1 pixel (~50 micron), then the position of the vector of the ray will change ~ 375 micron in the sample, ignoring the second detector distance.

Another reason can be that two grains with the same orientation will result in two spots very close together on the detector. These spots are not easy to distinguish and thus are the grains. In addition, it is possible that the wrong spots are assigned to a grain during indexing. Furthermore, the spots from the three detector distances can be wrongly related.

The method of ray-tracking was not used for the 3D reconstruction described in the next section.

Figure 7-14: Examples of the reconstruction of the center of mass of a grain in the 3DXRD sample. A) Relatively good fit: 1) Overview; 2) Enlarged side view; 3) Enlarged top view. B) Relatively bad fit: 1) Overview; 2) Enlarged side view; 3) Enlarged top view. In both examples the ‘rays’ traced from the spots on the detector at the three distances do not intersect at one center of mass, but form a cloud of intersections. In the relatively good fit, the cloud is denser than for the relatively bad fit. Scale of the axes: micrometers.
7.5 3D reconstruction

For the 3D reconstruction of the austenite structure with a Voronoi tessellation the spots from the diffraction patterns of the specimen are indexed according to the procedure described in section 7.4.2, with some additional steps, such as calculating the corresponding grain size for each spot and using only the spots on ring 2 as described in section 7.2.

Figure 7-15 shows the 3D reconstruction with a Voronoi tessellation of the FCC grains. However, with a basic Voronoi tessellation the calculated volume of the indexed grains is not included. The Voronoi grains are constructed around the centers of mass, where each grain boundary lies at the same distance from each neighboring center of mass.

Subsequently, the grain size for each grain is calculated as the average from the grain sizes of each spot assigned to this grain. Both the experimental and the Voronoi grain radii from the 297 indexed grains with an assumed spherical shape that fulfill the requirements of the filters are calculated. The grain radii are shown in Figure 7-16. The calculated grain volumes from the experiments are not taken into account during the Voronoi tessellation, resulting in a difference between the experimental and the Voronoi volumes of the grains and therefore between the experimental and Voronoi radii of the grains shown in Figure 7-16. It is observed that the experimental grain radii and the Voronoi radii do not correspond, as the graph in Figure 7-16C shows peaks and valleys instead of a steady line at zero. The shape of the graph of the experimentally found grain radii shows a large fluctuation in grain sizes, whereas the shape of the graph of the Voronoi radii is much smoother.

After the indexing, 86.5% of the illuminated volume of the sample is indexed. This explains why the calculated radii from the Voronoi tessellation is on average larger than the grain radii as calculated from the integrated intensities of the spots. The specimen space is completely filled in the Voronoi reconstruction.

In order to obtain a minimal difference between the experimental and the Voronoi radii, the grain volumes need to be taken into account during the Voronoi tessellation in addition to the position of the centre of mass. The many twins in the austenitic microstructure are difficult to represent by a Voronoi reconstruction. In reality, an FCC-grain can sometimes be enclosed by its twin-related neighbor. This is not possible to reproduce in a normal Voronoi tessellation.

In addition, the 3D reconstruction would be better when the calculated grain volumes are taken into account besides the center of mass. An even more realistic 3D reconstruction would be obtained when the twin-related grains could be reconstructed.

7.5.1 Grain orientation

In addition to the grain size and the centers of mass, the grain orientations can be calculated as well. In Figure 7-17 an Inverse Pole Figure (IPF) of the crystallographic orientations of the indexed grains in the illuminated volume of the sample. It is observed
that the IPF shows a maximum at the \{111\}-pole and a local maximum at the \{001\}-pole. It is already known that axi-symmetrically extruded and drawn products of FCC metals generally have major \(<111> + \text{minor } <001>\) double fiber textures in the deformed state [15]. However, the sample comprises deformed FCC metal that has been recrystallized. Nevertheless, it is known that sometimes the deformed texture is retained during recrystallization. Therefore, this reconstructed texture from the 3DXRD data is possible to occur in reality.

However, in order to check whether the crystallographic orientations of the grains have been correctly reconstructed from the 3DXRD data, the texture from the pole figure in Figure 7-17 should be compared to a pole figure of the sample obtained by EBSD.

In addition, two more requirements are added to the indexing process. For each grain, at least four spots must be found on the \{200\}-ring, with a maximum of six. All found spots then cannot have a larger difference in the represented grain radius than 5 µm. Furthermore, the Internal Angle, i.e. the error in the indexing, cannot be larger than 0.05°.

Based on the orientation of all the individual grains an inverse pole figure obtained from the 3DXRD microscopy, which corresponds to the texture typically found in drawn or swaged wire. The three-dimensional microstructure was estimated from the position of the center of mass of the individual grains in the specimen and a Voronoi reconstruction. A comparison between the volumes of the grains as calculated from the Voronoi reconstruction and the volume of the individual grains shows differences. It is recommended to include the volumes of the grains in the Voronoi reconstruction.

### 7.7 Acknowledgement

This chapter could not have been written without the help of the people of ID11 of the ESRF: Aleksei Bytchkov, Carsten Gundlach and Jonathan Wright; and the tremendous help of Richard Huizenga and Jette Oddershede and Søren Schmidt of Risø National Laboratory, Denmark.

### 7.8 References


**8. Summary**

*Nucleation of ferrite in austenite: The role of crystallography*

The grain nucleation mechanisms during solid-state phase transformations in polycrystalline materials are still not completely understood. The nucleation stage has a strong influence on the overall evolution of phase transformations and recrystallisation processes. This determines the final microstructure and thereby the properties of the material. The understanding of grain nucleation is important for controlling the production process, the design of new alloys with optimal properties, and the production of tailor-made alloys. Despite the worldwide scientific interest and technological relevance that has driven numerous studies on solid-state grain nucleation, the understanding of the underlying mechanisms is still limited. The scope of the thesis is to study the influence of crystallography on ferrite nucleation during the austenite/ferrite transformation in an iron-chromium-nickel (Fe-Cr-Ni) alloy and a cobalt-iron (Co-Fe) alloy.

In Chapter 2, solid-state nucleation is explained according to the classical nucleation theory and the experimental observations of several scientists in this field of Materials Science. The classical nucleation theory provides an expression for the time-dependent nucleation rate. The parameters in this expression are the density of potential nucleation sites, the frequency factor, the non-equilibrium Zeldovich factor, the activation energy for nucleation, the incubation time, the isothermal transformation time and the transformation temperature. Attention is given to the activation energy for nucleation that is directly influenced by the driving force for nucleation, the shape of the nucleus, the potential nucleation sites and the interface energies involved during nucleation. The driving force for nucleation is the difference in Gibbs free energy of the phases involved in the transformation. The spherical cap and the pillbox models for grain faces, grain edges and grain corners are introduced. The experimental observations include views on the potential nucleation sites, the nucleus shape and the influence of alloying elements on the activation energy for nucleation.

Chapter 3 concerns a description of the crystallographic orientation of the many grains in a metal and the interfaces that are formed between these grains. The methods of representing the crystallographic orientation are described, as well as the methods of representing misorientation, i.e. the difference in crystallographic orientation, between
Chapter 4 introduces the diffraction techniques used in for the experimental work in this thesis. First, the general theory of diffraction is described by Bragg's Law, which is a very important tool in texture research. Furthermore, the Electron Backscattering Diffraction (EBSD) is described. EBSD is a technique which allows to obtain crystallographic information from samples in a scanning electron microscope (SEM). An electron beam is diffracted by the lattices of a tilted crystalline sample and forms a Kikuchi pattern, consisting of Kikuchi bands, which is characteristic of the crystal structure and orientation of the illuminated volume. In addition, the technique of three-dimensional X-ray diffraction microscopy (3DXRD) is described. Hard X-rays from a synchrotron source have such high energies that it is possible to be transmitted through 5 mm of steel. 3DXRD uses a monochromatic high-energy X-ray beam to penetrate a steel sample, which is positioned on a table that is rotated over an angle $\Delta \omega$ with steps of $\Delta \omega$. The X-ray beam is diffracted by the lattices in the sample, resulting in diffraction patterns that are caught by the detector. A diffraction pattern consists of individual spots. Each spot represents a single grain. Depending on the kind of experiment, information about the position, the crystal structure and crystallographic orientation of the grains can be obtained from the position of the spots after post-processing. A method for this post-processing is described as well.

Chapter 5 investigates the role of grain and phase boundary misorientations during nucleation of ferrite in austenite, as well as the effect of a slight deformation of the austenite matrix on the density of ferrite nuclei that form during subsequent isothermal annealing. EBSD was performed on a high purity iron alloy with 20 wt.\% Cr and 12 wt.\% Ni with austenite and ferrite stable at room temperature so that the crystallographic misorientation between austenite grains and between ferrite and austenite grains can be identified. Two specimens are annealed at $1400^\circ$C for different time periods. Another specimen is slightly deformed and subsequently annealed at $1400^\circ$C. It is observed that almost 90% of all observed ferrite grains in the three specimens have a specific orientation relationship with at least one austenite grain or at least along part of the phase boundary, which implies that the specific orientation relationship plays an important role during solid-state nucleation of ferrite. Ferrite nucleation is observed at triple junctions (grain edges or corners), at grain faces, and within a grain (intragranular nucleation). Ferrite grains nucleate on grain faces independently of the misorientation between austenite grains, although random high-angle grain boundaries have a slightly higher efficiency compared to low-angle grain boundaries and twin boundaries. Different types of nucleation mechanisms are found to be simultaneously active during ferrite formation at grain faces, which can be related to the theory of Clemm and Fisher, the coherent pillbox model, and the pillbox-cum-spherical-cap model. A slight deformation of the austenite matrix was found to triple the number of ferrite nuclei during isothermal annealing. The observed low angle grain boundary (LAGB) structure in the deformed specimen is induced by the deformation and not by the nucleation process itself because the nucleation of ferrite grains during annealing in the absence of externally imposed plastic strain does not lead to the formation of additional low-angle grain boundaries.

Chapter 6 investigates the role of crystallographic misorientations during nucleation of body centered cubic (BCC) grains on face centered cubic (FCC) grain boundary faces. 3D-EBSD is performed on a cobalt alloy with 15 wt.\% Fe, which was heat-treated to have a microstructure with small BCC grains on FCC grain boundaries. The 3D-EBSD makes it possible to study the formation of multiple nuclei at the same grain boundary face. Variant selection during the formation of multiple nuclei at the same grain boundary face is investigated. It is observed that the specific orientation relationships between ferrite and austenite play a dominant role during solid-state nucleation of ferrite. In addition, no BCC grains nucleated on twin boundaries, which represented more than half of the total FCC/FCC boundary length. Three types of BCC nuclei have been found. BCC nuclei without a specific orientation relationship with any of the two neighboring FCC grains, BCC nuclei with a specific orientation relationship with only one of the two neighboring FCC grains, and BCC nuclei with a specific orientation relationship with both neighboring FCC grains. All the BCC-nuclei having a specific orientation relationship with both neighboring FCC-grains form on incoherent high-energy FCC/FCC grain boundaries. This does not correspond to the coherent pillbox model. A modified pillbox model is presented. In case the BCC grains have an orientation relationship with both neighboring FCC grains and are located on
the same FCC/FCC grain boundary face, it is observed that these BCC grains have the same crystallographic orientation within 5°. This small angular deviation means that only one variant of the specific orientation relationships is selected during nucleation of these BCC grains. In case a BCC-grain is present on an FCC/FCC grain boundary face (GBF) having an orientation relationship with both parent grains, the majority of the nuclei on that GBF will nucleate according to this variant. In case the BCC grains have an orientation relationship with only one FCC parent grain and are located on the same FCC/FCC grain boundary face, it is found that different variants are present on the same FCC grain boundary face. We have observed one BCC grain that nucleated without a specific orientation relation with either of the two austenite grains on the same FCC/FCC grain boundary face at which we observed ten BCC grains that nucleated with a specific orientation relation with both FCC-grains. This shows that the activation energy for nucleation of a BCC-nucleus having an orientation relation with both FCC-grains is lower than the activation energy for nucleation of a BCC-nucleus without an orientation relation with either of the FCC-grains. The FCC/FCC grain boundary faces that facilitated nucleation of BCC nuclei with a specific orientation have a specific misorientation angle, corresponding with the misorientation angles between the variants of the specific orientation relationships.

Chapter 7 describes 3DXRD-measurements that were performed at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France and the development of data-analysis strategies to determine the 3D microstructure of austenite without destroying the specimen. Measurements are performed on the same alloy as described in chapter 5, i.e. the Fe-20Cr-12Ni alloy. The austenite phase is investigated by 3DXRD. Since austenite contains many twin-related grains, the diffraction of two twin-related austenite grains is simulated. It is observed that the diffraction of twin-related grains can cause severe errors in the indexing as the diffraction spots on the {111}-, {220}-, {311}- and {222}-rings of these grains overlap. On the {220}- and {311}-rings 50% of the spots overlap. From the simulation it is clear that only for the {200}-plane no overlap in the spots can be observed. Therefore, the indexing of the grains is performed with only the spots on the {200}-ring. In addition, two more requirements are added to the indexing process. For each grain a maximum of six spots is available of which at least four spots must be found on the {200}-ring for a successful indexing. In addition, all found spots then cannot have a larger than 5 µm difference in the represented grain radius. Furthermore, the Internal Angle (IA), i.e. a measure for the error in the indexing, cannot be larger than 0.05°. Based on the orientation of all the individual grains an inverse pole figure obtained from the 3DXRD microscopy, which corresponds to the texture typically found in drawn or swaged wire. The three-dimensional microstructure was estimated from the position of the center of mass of the individual grains in the specimen and a Voronoi reconstruction. A comparison between the volumes of the grains as calculated from the Voronoi reconstruction and the volume of the individual grains shows differences. It is recommended to include the volumes of the grains in the Voronoi reconstruction.

Hiske Landheer
Delft, October 2010
9. Samenvatting

Kieming van ferriet in austeniet: De rol van kristallografie

De mechanismes achter korenlkieming tijdens vaste-stof faseveranderingen in polykristalline materialen zijn nog steeds niet volledig begrepen. Het kiemstadium heeft veel invloed op de algehele ontwikkeling van faseveranderingen en rekristallisatieprocessen. Dit bepaalt de uiteindelijke microstructuur en daarmee de eigenschappen van het materiaal. Begrip van het kiemmechanisme is belangrijk voor de beheersing van het productieproces, de ontwikkeling van nieuwe legeringen met optimale eigenschappen en de productie van op maat gemaakte legeringen. Ondanks de wereldwijde wetenschappelijke interesse en technologische relevantie, vaak de drijvende kracht achter studies naar vaste-stof korenlkieming, is het begrip van het onderliggende mechanisme nog steeds beperkt. Het doel van dit proefschrift is het bestuderen van de invloed van kristallografie op ferrietkieming tijdens de austeniet-ferriettransformatie in een ijzer-chroom-nikkel (Fe-Cr-Ni) legering en een kobalt-ijzer (Co-Fe) legering.

In Hoofdstuk 2 wordt vaste-stofkieming uitgelegd met behulp van de klassieke kiemtheorie en de experimentele observaties van verschillende wetenschappers in het vakgebied van de Materiaalkunde. De klassieke kiemtheorie voorziet in een vergelijking voor de tijdsafhankelijke kiemnelheid. De parameters in deze vergelijking omvatten de dichtheid van potentiële kiemplaatsen, de frequentiefactor, de niet-evenwichtsfactor van Zeldovich, de kiemingsactiveringsenergie, de incubatietijd, de potentiële kiemplaatsen en de grensvlakenergieën.

Hoofdstuk 3 betreft een beschrijving van de kristallografische oriëntatie van de korens in een metaal en de grensvlakken die worden gevormd tussen deze korens. De weergavemethoden voor de kristallografische orientatie worden beschreven, evenals de weergavemethoden voor de misoriëntatie – het verschil in kristallografische orientatie tussen twee korens. Grensvlakken kunnen verschillende structuren en geometriën hebben, die de korrelgrensenergie beïnvloeden. Het grensvlak tussen twee verschillende fasen kan soms worden beschreven met een specifieke oriëntatierelatie. Deze specifieke oriëntatierelaties hebben ook een grote invloed op de energieën op deze fasegrenzen en daarbij op de kieming van de nieuwe fase. Uit simulaties is bekend dat fasegrenzen met een specifieke oriëntatierelatie lagere korrelgrensenergie hebben dan fasegrenzen met een willekeurige misoriëntatie. De grensvlakenergie is afhankelijk van zowel de misoriëntatieals van de hellingshoek van het korrelgrensvlak.

Hoofdstuk 4 introduceert de diffratietechieken die zijn gebruikt voor het experimentele werk van dit proefschrift. Als eerste wordt de algemene diffratietheorie beschreven met de Wet van Bragg, die een belangrijk instrument is in het textuuronderzoek. Verder wordt Electron Backscattering Diffraction (EBSD) beschreven. EBSD is een techniek, waarbij kristallografische informatie van proefstukken in een Scanning Elektronenmicroscoop (Scanning Electron Microscope, SEM) kan worden verkregen. Een elektronbundel wordt gediffracteerd door het rooster van een kristallijn proefstuk en vormt een Kikuchipatroon bestaande uit Kikuchibanden, die karakteristiek is voor de kristalstructuur en kristallografische orientatie van het bestraalde volume.

In Hoofdstuk 5 onderzoekt de rol van korrel- en fasegrensmisoriëntaties tijdens de kieming van ferriet in austeniet, evenals het effect van een lichte vervorming van de austenietmatrix op de dichtheid van de ferriekiemten die worden gevormd tijdens de daaropvolgende isotherme warmtebehandeling. EBSD is toegepast op een hoogzuivere ijzerlegering met 20 gew.% Cr en 12 gew.% Ni met austeniet en ferriet als stabiele fasen op kamertemperatuur, zodat de kristallografische misoriëntaties hebben, die de korrelgrensenergie beïnvloeden. Het grensvlak tussen twee verschillende fasen kan soms worden beschreven met een specifieke orientatierelatie. Deze specifieke oriëntatierelaties hebben ook een grote invloed op de energieën op deze fasegrenzen en daarbij op de kieming van de nieuwe fase. Uit simulaties is bekend dat fasegrenzen met een specifieke oriëntatierelatie lagere korrelgrensenergie hebben dan fasegrenzen met een willekeurige misoriëntatie. De grensvlakenergie is afhankelijk van zowel de misoriëntatie als van de hellingshoek van het korrelgrensvlak.
tussen de austenietkorrels en tussen de ferriet- en austenietkorrels kunnen worden vastgelegd. Twee proefstukken zijn op 1400°C warmtebehandeld gedurende verschillende tijdsperoides. Een ander proefstuk is licht vervormd en daaropvolgend warmtebehandeld op 1400°C. Uit waarnemingen blijkt dat bijna 90% van alle waargenomen ferrietkorrels in de drie proefstukken een specifieke oriëntatierelatie hebben met ten minste een austenietkorrel of ten minste langs een gedeelte van de fasegrens, wat inhoudt dat de specifieke oriëntatierelatie een belangrijke rol speelt tijdens de vaste-stijkstraai van ferriet. Ferrietkieming is waargenomen op driesprongen (triple junctions), die korrelranden of korrelhoeken kunnen voorstellen, op korrelvlakken en binnenin een korrel (intragranulaire kieming). Ferrietkorrels kiemen op korrelvlakken onafhankelijk van de misoriëntatie tussen de austenietkorrels, hoewel willekeurige grote-hoekkorrelgrenzen een licht hogere efficiëntie hebben vergeleken met kleine-hoekkorrelgrenzen en tweelinggrenzen. Het blijkt dat verschillende kiemmechanismen tegelijkertijd actief zijn op korrelvlakken tijdens de ferrietvorming, welke gerelateerd kunnen worden aan de theorie van Clemm en Fisher, het cohereente pillendoosmodel en de pillendoos-met-bolkap-model. Een lichte vervorming van de austenietmatrix blijkt het aantal ferrietkiemen tijdens de warmtebehandeling te verdrievoudigen. De waargenomen kleine-hoekkorrelgrensstructuur in het vervormde proefstuk is veroorzaakt door de vervorming en niet door het kiemproces zelf, omdat de ferrietkieming tijdens de warmtebehandeling zonder extern opgelegde plastische vervorming niet leidt tot de vorming van meer kleine-hoekkorrelgrenzen.

Hoofdstuk 6 onderzoekt de rol van kristallografische misoriëntaties tijdens de kieming van kubisch ruimtelijk gecentreerde (KRG) korrels op kubisch vlakgecentreerde (KVG) korrelgrens. Driedimensionale EBSD (3D-EBSD) is toegestaan op een kobaltlegering met 15 gew.% ijzer (Fe), dat is warmtebehandeld voor de verkrijging van de 3D microstructuur van austeniet zonder de vernietiging van het proefstuk. De metingen zijn uitgevoerd op dezelfde legering als beschreven in Hoofdstuk 5, de 3DXRD-experimenten die zijn uitgevoerd op de Europese Synchrotronstraling Faciliteit (European Synchrotron Radiation Facility, ESRF) in Grenoble, Frankrijk, en de ontwikkeling van data-analyse strategieën voor het bepalen van de 3D microstructuur van austeniet zonder de vernietiging van het proefstuk.
50% van de stippen. Uit de nabootsing wordt duidelijk dat alleen in geval van de {200}-ring geen overlap is waar te nemen. Daarom wordt de ‘indexing’ van de stippen uitgevoerd met enkel de stippen op de {200}-ring. Daarnaast zijn nog twee vereisten toegevoegd aan het ‘indexing’-proces. Voor elke korrel is een maximum van zes stippen voorhanden, waarvan ten minste vier stippen gevonden moeten worden op de {200}-ring voor een geslaagde ‘indexing’. Bovendien mogen alle gevonden stippen geen groter verschil dan 5 μm in korreldiameter hebben. Daarnaast mag de ‘Internal Angle’ (IA) – een maat voor de fout in de ‘indexing’ – niet groter zijn dan 0.05°. Op basis van de oriëntatie van alle individuele korrels is een Inverse Poolfiguur (IPF) gemaakt van de 3DXRD microscopie, welke overeenkomt met de textuur die karakteristiek is voor getrokken of gesmeed draad. De driedimensionale microstructuur is berekend met behulp van de massamiddelpunten van de individuele korrels in het proefstuk en een Voronoi-reconstructie. Een vergelijking tussen de berekende volumes van de korrels in de Voronoi-reconstructie en de volumes van de individuele korrels uit de experimentele data toont een aantal verschillen. Het is aan te raden de experimenteel gevonden volumes van de korrels mee te nemen in de Voronoi-reconstructie.

Hiske Landheer

Delft, oktober 2010
10. Acknowledgements

In the many years that I have spent at the Delft University of Technology, I have seen many people come and go. Now it is my time to go and that goes with saying a big THANK YOU to some people.

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Somebody used to tell me that there are three conditions for a good PhD: sufficient funding, good supervision and a subject of interest. I can say that I have had all three of them. The people that are responsible for that are:

My daily supervisor and copromotor Erik Offerman – years ago, Erik asked me for a PhD. Although I hesitated in the beginning, I have not regretted that I said yes. Thank you for these years and for always listening to me, even when I wasn't talking about science. Thank you for believing in me and for giving me faith when I did not believe I could do it anymore, and the trust to do things my way.

My promotor Leo Kestens – our first meeting was in Ghent. I still remember this first introduction into texture, a new but important field for me then. I have really appreciated our discussions about (materials) science, the differences between Belgium and Holland, history, books and even philosophy. I am going to miss that. Thank you for your trust and faith in me and for encouraging me.

Other MCM-members need some more attention as well: Roumen Petrov – without you the fundamentals of this thesis would not be as strong: thank you for the many EBSD scans from Ghent; Richard Huizenga – you are amazing with software. I still don’t know how you do it, but without your skills Chapter 7 would have been an even tougher chapter; Jilt Sietsma – thank you for your bold action to get me to finish this thesis, I guess I needed that extra bit; Nico Geerlofs – thank you for your assistance in
the dilatometry experiments; Erik Peekstok – thanks for the assistance with the cutting, polishing and etching of my many samples and with the microscope.

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Outside of MCM, but still within the safe haven of the Materials Science and Engineering department, are some people that need a thank you: Niek van de Pers, Kees Kwakernaak and Han Kiers have contributed to this thesis with their knowledge of and assistance with X-ray diffraction and electron microscopy.

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Furthermore, I would like to thank Sietske Geuzebroek again for writing an excellent literature review and for kindly letting me use this as a basis for Chapter 2. My gratitude also goes out to Prof. W.B. Hutchinson of KTH Stockholm for the discussions on chapter 5 and the resulting paper in Acta Materialia. Professor Enomoto: thank you for letting me stay in your group at Ibaraki University in Hitachi, Japan, and to work with you.

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Outside the world of materials science, there were my family and friends. To all of them who kept an interest in my doings, even though it was sometimes hard to understand what is was and why: Thank you for your regular questions on how and what I was doing. I hope this book will explain things a bit.

My friends Jantine, Jessica, Lisan, Leonie, Saskia en Thamar – I am grateful for your friendship through the years, from our teens to our busy grown-up lives. I hope we can share many more years of friendship.

Jolanda – we have known each other for many years now. I can already imagine us when we are old, happily remembering the days of our lives. Thank you for being my friend and for sharing this special day.

My (little) sister Kristien – you have been my best friend my whole life. We now have our own grown-up lives and families, but the bond between sisters remains. I am so grateful for your help making this thesis into a real book! Thank you for being there and for who you are.

My parents, Yolande and Huib – you have given us a carefree and loving childhood. Without your love and faith, I would not have come this far. Your confidence in me and my abilities always put me back on track. Thank you for your enduring support.

Now I have come to the two most important people in my life: Thim, my love, my soulmate – I owe you big time for your love, support and patience during these years, especially these last months; and Matteo, our sunshine and little angel – you are the best gift ever. Without you two my world would be an empty place. I love you.

I was just guessing at numbers and figures, pulling the puzzles apart

Questions of science, science and progress
do not speak as loud as my heart

(‘The Scientist’ by Coldplay)
************
11. About the author

Hiske Landheer was born on 6 August 1980 in Zuid-Beijerland in the Netherlands. After her Athenaeum at the CSG Willem van Oranje in Oud-Beijerland, she embarked on her studies in Materials Science and Engineering at Delft University of Technology in 1998 and in 2004 she obtained her M.Sc. degree.

In September of that same year, she started her PhD research in the group of Microstructural Control in Metals (MCM) of the Department of Materials Science and Engineering (MSE) of the Faculty of Mechanical, Maritime and Materials Engineering (3ME) under supervision of Prof.Dr.ir. Leo Kestens and Dr.ir. Erik Offerman.

She is currently a trainee patent attorney at Nederlandsch Octrooibureau in The Hague, the Netherlands.

Publications


This appendix contains more information on the crystallographic orientations of the BCC and FCC grains described in Chapter 6. In addition, an overview of the misorientations between either BCC grains or FCC grains is given. The table captions refer to the figures in Chapter 6.

Table A-1: Orientation and orientation spread of the BCC grains shown in figure 6-3.

<table>
<thead>
<tr>
<th>BCC grain</th>
<th>Orientation</th>
<th>Spread</th>
</tr>
</thead>
<tbody>
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<td>P1</td>
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<td>18.7</td>
</tr>
<tr>
<td>P2</td>
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<td>P3</td>
<td>180.2</td>
<td>18.3</td>
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<td>P4</td>
<td>182.9</td>
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<td>P5</td>
<td>186.9</td>
<td>18.6</td>
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<tr>
<td>P8</td>
<td>191.5</td>
<td>19.2</td>
</tr>
<tr>
<td>P9</td>
<td>192.0</td>
<td>18.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
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<th>Orientation</th>
<th>Spread</th>
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</thead>
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<tr>
<td>P16</td>
<td>176.1</td>
<td>27.2</td>
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</table>

Table A-2: Orientation and orientation spread for the FCC grains in Figure 6-3.

<table>
<thead>
<tr>
<th>FCC grain</th>
<th>Orientation (Euler angles)</th>
<th>Spread</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1</td>
<td>153.3</td>
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<td>E2</td>
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<tr>
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<td>25.7</td>
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Table A-3: Misorientation angles between each precipitate (P) and each EBSD scan in Figure 6-3.

<table>
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<td>P5-P8</td>
<td>1.8°</td>
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<td>P6-P9</td>
<td>2.4°</td>
<td>P9-P15</td>
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<td>P7-P9</td>
<td>1.7°</td>
<td>P10-P14</td>
<td>1.7°</td>
<td>P14-P17</td>
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<td>P7-P10</td>
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<td>P7-P11</td>
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<td>P15-P16</td>
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<td>P8-P9</td>
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<td>P11-P13</td>
<td>3.7°</td>
<td>P15-P17</td>
<td>3.1°</td>
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<td>P8-P10</td>
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<td>P11-P14</td>
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<td>P15-P18</td>
<td>3.8°</td>
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<td>0.4°</td>
<td>P11-P15</td>
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<td>3.2°</td>
<td>P8-P12</td>
<td>2.1°</td>
<td>P12-P13</td>
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<td>P16-P18</td>
<td>11.2°</td>
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<tr>
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<td>1.3°</td>
<td>P8-P13</td>
<td>2.7°</td>
<td>P12-P14</td>
<td>1.9°</td>
<td>P17-P18</td>
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Table A-4: Average misorientation angle between the FCC grains and the spread of this misorientation angle of the EBSD scans shown in Figure 6-3.

<table>
<thead>
<tr>
<th>FCC grain boundary</th>
<th>Average misorientation</th>
<th>Spread</th>
</tr>
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<tbody>
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<td>E1 1-2</td>
<td>56.2°</td>
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</tr>
<tr>
<td>E2 1-2</td>
<td>56.4°</td>
<td>0.3°</td>
</tr>
<tr>
<td>E2 1-3</td>
<td>25.5°</td>
<td>0.8°</td>
</tr>
<tr>
<td>E3 1-2</td>
<td>56.2°</td>
<td>0.9°</td>
</tr>
<tr>
<td>E3 1-3</td>
<td>25.8°</td>
<td>0.3°</td>
</tr>
<tr>
<td>E4 1-2</td>
<td>56.1°</td>
<td>2.1°</td>
</tr>
<tr>
<td>E4 1-3</td>
<td>25.8°</td>
<td>1.3°</td>
</tr>
<tr>
<td>E5 1-3</td>
<td>26.3°</td>
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</tr>
<tr>
<td>E5 1-4</td>
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Table A-5: Orientation and orientation spread of the BCC grains shown in figure 6-4

<table>
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<th>BCC grain</th>
<th>Orientation (Euler angles)</th>
<th>Spread</th>
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<tbody>
<tr>
<td>P1</td>
<td>198.3 41.0 200.2</td>
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<tr>
<td>P2</td>
<td>206.7 30.7 192.9</td>
<td>0.8</td>
</tr>
<tr>
<td>P3</td>
<td>142.2 39.7 195.8</td>
<td>0.5</td>
</tr>
<tr>
<td>P4</td>
<td>145.0 38.0 190.5</td>
<td>0.7</td>
</tr>
<tr>
<td>P5</td>
<td>145.6 38.3 189.3</td>
<td>0.7</td>
</tr>
<tr>
<td>P6</td>
<td>145.5 39.6 195.2</td>
<td>0.4</td>
</tr>
<tr>
<td>P7</td>
<td>344.6 52.7 347.9</td>
<td>0.3</td>
</tr>
<tr>
<td>P8</td>
<td>146.5 39.1 194.1</td>
<td>0.5</td>
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<tr>
<td>P9</td>
<td>145.9 38.2 194.5</td>
<td>0.6</td>
</tr>
<tr>
<td>P10</td>
<td>149.7 36.1 187.6</td>
<td>0.7</td>
</tr>
<tr>
<td>P11</td>
<td>199.3 41.5 200.6</td>
<td>0.5</td>
</tr>
<tr>
<td>P12</td>
<td>341.3 53.1 351.1</td>
<td>0.8</td>
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<td>P13</td>
<td>341.3 53.1 351.1</td>
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<td>P14</td>
<td>206.3 30.4 195.4</td>
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<tr>
<td>P15</td>
<td>339.4 53.2 353.6</td>
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Table A-6: Orientation and orientation spread for the FCC grains in Figure 6-4.

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<th>Spread</th>
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</thead>
<tbody>
<tr>
<td>E1 1</td>
<td>146.2 56.3 229</td>
<td>0.5</td>
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<tr>
<td>E4 6</td>
<td>147.8 54.8 229.2</td>
<td>0.6</td>
</tr>
<tr>
<td>E1 2</td>
<td>206.5 52.8 137.4</td>
<td>0.6</td>
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<tr>
<td>E1 3</td>
<td>213.8 40.7 142.7</td>
<td>0.8</td>
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<tr>
<td>E2 3</td>
<td>217.3 41.1 141.1</td>
<td>0.9</td>
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<td>E3 3</td>
<td>218.3 41.4 139.9</td>
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<td>209.2 46.2 145.6</td>
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<td>E4 5</td>
<td>208.1 47.3 145.9</td>
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</tbody>
</table>

Table A-7: Misorientation angles between each precipitate from each EBSD scan in Figure 6-4.

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<td>P1 – P4</td>
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<tr>
<td>P1 – P5</td>
<td>49.8°</td>
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<tr>
<td>P1 – P7</td>
<td>54.3°</td>
</tr>
<tr>
<td>P1 – P8</td>
<td>53.9°</td>
</tr>
<tr>
<td>P2 – P3</td>
<td>51.6°</td>
</tr>
<tr>
<td>P2 – P4</td>
<td>47.3°</td>
</tr>
<tr>
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<td>P2 – P6</td>
<td>53.4°</td>
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<td>P2 – P7</td>
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</tr>
<tr>
<td>P2 – P8</td>
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<td>P3 – P4</td>
<td>3.8°</td>
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<tr>
<td>P3 – P5</td>
<td>4.2°</td>
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<tr>
<td>P11 - P12</td>
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Table A-8: Average misorientation angle between the FCC grains and the spread of this misorientation angle of the EBSD scans shown in Figure 6-4.

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<th>Spread</th>
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<tbody>
<tr>
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<tr>
<td>E2 3-4</td>
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<td>1.3°</td>
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<tr>
<td>E3 3-4</td>
<td>17.1°</td>
<td>1.1°</td>
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Table A-9: Orientation and orientation spread for the FCC grains in Figure 6-5.

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<td>E7 1</td>
<td>174.3 13.8 252.4 0.8</td>
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<tr>
<td>E6 2</td>
<td>159.0 27.1 172.9 0.4</td>
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<tr>
<td>E7 2</td>
<td>332.5 63.0 3.4 0.5</td>
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Table A-10: Orientation and orientation spread of the BCC grains shown in figure 6-5

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<tr>
<td>P2</td>
<td>142.1 18.9 236.3 0.5</td>
<td></td>
</tr>
<tr>
<td>P3</td>
<td>141.3 19.0 237.3 0.5</td>
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</tr>
<tr>
<td>P4</td>
<td>144.4 18.3 235.1 0.4</td>
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</tr>
<tr>
<td>P5</td>
<td>142.6 18.6 236.9 0.7</td>
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<tr>
<td>P6</td>
<td>272.8 21.2 93.0 1.3</td>
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</tr>
<tr>
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<td>142.4 19.1 237.4 0.5</td>
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<tr>
<td>P8</td>
<td>142.7 19.0 237.3 0.4</td>
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<tr>
<td>P9</td>
<td>140.9 19.4 239.1 0.5</td>
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<td>141.4 19.9 239.0 0.4</td>
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<td>P11</td>
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Table A-11: Misorientation between each precipitate of each EBSD scan in Figure 6-5.

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<td>1.3°</td>
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<tr>
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<td>1.9°</td>
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<tr>
<td>P1 – P6</td>
<td>38.5°</td>
</tr>
<tr>
<td>P1 – P7</td>
<td>1.7°</td>
</tr>
<tr>
<td>P1 – P8</td>
<td>1.6°</td>
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<tr>
<td>P1 – P9</td>
<td>1.9°</td>
</tr>
<tr>
<td>P1 – P10</td>
<td>3.0°</td>
</tr>
<tr>
<td>P1 – P11</td>
<td>2.6°</td>
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<tr>
<td>P2 – P3</td>
<td>0.7°</td>
</tr>
<tr>
<td>P2 – P4</td>
<td>1.5°</td>
</tr>
<tr>
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<td>1.2°</td>
</tr>
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<td>39.4°</td>
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<tr>
<td>P2 – P8</td>
<td>1.2°</td>
</tr>
<tr>
<td>P2 – P9</td>
<td>1.5°</td>
</tr>
<tr>
<td>P2 – P10</td>
<td>2.1°</td>
</tr>
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<td>P2 – P11</td>
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</table>

<table>
<thead>
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<th>Precipitates</th>
<th>Misorientation</th>
</tr>
</thead>
<tbody>
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<td>1.4°</td>
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<tr>
<td>P3 - P6</td>
<td>39.4°</td>
</tr>
<tr>
<td>P3 - P7</td>
<td>1.0°</td>
</tr>
<tr>
<td>P3 - P8</td>
<td>1.0°</td>
</tr>
<tr>
<td>P3 - P9</td>
<td>1.6°</td>
</tr>
<tr>
<td>P3 - P10</td>
<td>2.3°</td>
</tr>
<tr>
<td>P3 - P11</td>
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</tr>
<tr>
<td>P5 - P8</td>
<td>0.5°</td>
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<tr>
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<td>P6 - P10</td>
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<tr>
<td>P6 - P11</td>
<td>41.1°</td>
</tr>
<tr>
<td>P7 - P8</td>
<td>39.8°</td>
</tr>
<tr>
<td>P7 - P9</td>
<td>40.5°</td>
</tr>
<tr>
<td>P7 - P10</td>
<td>41.1°</td>
</tr>
<tr>
<td>P7 - P11</td>
<td>41.1°</td>
</tr>
</tbody>
</table>

Table A-12: Average misorientation angle between the FCC grains and the spread of this misorientation angle of the EBSD scans shown in Figure 1-5.

<table>
<thead>
<tr>
<th>FCC grain boundary</th>
<th>Average misorientation</th>
<th>Spread</th>
</tr>
</thead>
<tbody>
<tr>
<td>E6 1-2</td>
<td>14.6°</td>
<td>1.8°</td>
</tr>
<tr>
<td>E7 1-2</td>
<td>14.3°</td>
<td>1.7°</td>
</tr>
</tbody>
</table>
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