**In-situ** characterization of grain nucleation and coarsening in metallic microstructures using synchrotron radiation
The research described in this thesis was performed in the department of Materials Science and Engineering, of the Delft University of Technology, Delft, The Netherlands.

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Printed in the Netherlands
This thesis is dedicated to
H.H. Shri Bhola Nathji Bhagwan
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CHAPTER 1

INTRODUCTION

Most metals in use are polycrystals: aggregates of multiple crystals (grains), each with a different crystallographic orientation. The size distribution, spatial distribution and crystallographic orientation distribution of these grains have a direct influence on the mechanical properties of the material. For example, the Hall–Petch relationship shows that the strength of a material is directly proportional to the inverse of the square root of the average grain size \([1, 2]\). During manufacture, the evolution of the microstructure is controlled mainly by: (i) grain nucleation and grain growth during phase transformations; (ii) grain coarsening at high temperatures and; (iii) deformation characteristics including recrystallization. Even though numerous efforts have been made, the understanding of these three processes in metals is not yet complete. A major contributing factor to this has been the lack of suitable experimental techniques, which allow for \textit{in situ} studies.

The advancement of 3\textsuperscript{rd} generation synchrotron sources has opened up vast opportunities in materials research, especially due to the \textit{non-destructive} nature of the techniques. In particular for polycrystals, a number of techniques, such as X–Ray Phase–Contrast Tomography (PCT) \([3]\), Differential Aperture X–Ray Microscopy (DAXM) \([4]\), Three–Dimensional X–Ray Diffraction (3DXRD) microscopy \([5]\) and Diffraction Contrast Tomography (DCT) \([6, 7]\) have been used. 3DXRD is very promising for \textit{in situ} studies of polycrystalline materials during thermo–mechanical processing due to the unique combination of material properties that can be measured, namely: position, crystallographic orientation, volume and strain.
1. Introduction

state of the individual grains, which can be determined in a non-destructive manner. However, in order to extend the 3DXRD technique from its present state of a few demonstrative examples to being applied for tracking of statistically-relevant number of grains with a good time resolution during solid-state phase-transformations, at least two major shortcomings need to be overcome: (i) the limitations posed by the setup of the 3DXRD technique on the design of suitable furnaces for carrying out controlled heat treatments on the materials and; (ii) the limitations on the reduction / analysis of data acquired from specimen consisting of thousands of grains using 3DXRD.

At high temperatures, grains in polycrystalline materials grow in order to reduce the total interface energy of the system. According to the general theory of grain coarsening [8], the average grain size during isothermal annealing should be directly proportional to the square root of the annealing time. However, this relationship is very rarely observed, even for ultra-pure metals, with most experiments showing a faster decay in the rate of grain coarsening (the exponent for time is smaller than 0.5). This effect is commonly attributed to solute drag (slowing down of grain boundaries by solute atoms present in the matrix), to non-regular microstructures or to the presence of texture [2]. However, even after incorporating all the aforementioned factors, models for accurately predicting the rate of grain growth are non-existent.

As compared to the number of experiments carried out on grain coarsening, experimental observations of the process of solid-state nucleation are far too few, the main limitation being the difficulty in obtaining information about all the parameters affecting the nucleation rate. In particular, the activation energy for nucleation, which determines the barrier to nucleate, is very difficult to determine. The first efforts were calculations by Clemm and Fisher, who showed that the effectiveness of the potential nucleation sites is highest for grain corners, followed, in order, by nucleation at grain edges, faces and intra-granular nucleation [9]. A study by Lange et al. [10] on the nucleation rate of ferrite (\(\alpha\)) in austenite (\(\gamma\)) revealed that the activation energy for nucleation was much smaller than that predicted by the models of Clemm and Fisher [9], which Lange et al. [10] reasoned by using low energies of the \(\alpha-\gamma\) interfaces, which are created during nucleation.

In a recent study using synchrotron radiation, Offerman et al. [11] concluded that the activation energy for the nucleation of \(\alpha\) in \(\gamma\) was even lower by two orders of magnitude than that calculated by Lange et al. [10]. Similarly, Savran et al. [12] showed the same to be the case during nucleation of \(\gamma\) in \(\alpha\) during heating.
However, in both the studies of Offerman *et al.* [11] and Savran *et al.* [12], an overall activation energy was calculated because information about the position of the nuclei in the matrix and the crystallographic orientation of the grains could not be obtained. In reality, the total nucleation rate is the sum of the nucleation rates at different types of potential nucleation sites.

### 1.1 Technological relevance

Studying nucleation, growth and coarsening is of importance not only during the production of steels (to control the final microstructure), but also during the use of steels in high temperature applications such as fire–resistant steels or steels for energy conversion systems. The conventional method to improve the strength of steels for use at high temperatures (and to reduce the rate of grain coarsening at high temperatures during production) is to introduce precipitates with high number densities, which hinder the movement of grain boundaries and of dislocations during mechanical deformation. However, precipitates have two obvious disadvantages: (*i*) due to the increased rates of coarsening as temperatures are increased, the number density, and thus the effectiveness in pinning the grain boundaries, of the precipitates decreases and; (*ii*) easier dislocation climb and glide at higher temperatures reduces the effectiveness of precipitates themselves. This thesis investigates the changes occurring at the level of individual grains during heating and during annealing at high temperatures, which can then be used to design steels with optimized properties for application at high temperatures and control the final microstructure during production. The results presented in this thesis, albeit of a fundamental nature, have direct relevance for the design and the production steels for applications at high temperatures.

### 1.2 Aim of the thesis

The aim of the thesis is two–fold:

(*i*) To extend the application of synchrotron techniques, specifically 3DXRD microscopy, to study microstructural processes in metallic alloys. This includes overcoming the limitations of the technique, such as difficulties in carrying out accurate heat treatments, limited number of grains that can be observed, limitations due to the data analysis etc. However, instrumentation related issues, such as detector resolution, response time etc., are not investigated.
1. Introduction

**(ii)** To apply 3DXRD to enhance our understanding of two fundamental processes in metals: grain nucleation and grain coarsening.

1.3 Contents of the thesis

The thesis is divided into two parts: Chapters 2, 3 and 4 dealing with the improvements made to the 3DXRD technique and; Chapters 5, 6 and 7 describing the added insight obtained on the fundamental processes of grain nucleation and coarsening in model iron–based alloys.

Chapter 2 details a special furnace developed for the 3DXRD type of experiments. The furnace conforms to all the requirements of the synchrotron radiation technique as well as the qualities required for conducting research on polycrystalline materials during heat treatments.

Chapters 3 and 4 describe a software framework for the pre-processing of 3DXRD data (Chapter 3) and the techniques to obtain grain-specific information about volume, centre-of-mass position, crystallographic orientation and strain state (Chapter 4) simultaneously for thousands of grains. The software techniques developed are faster when handling more grains than other technique for the analysis of 3DXRD data.

Chapter 5 describes unique experiments on the coarsening of $\gamma$ grains in a model Fe–2 wt% Mn alloy at 1000 °C. By combining information about the volume, average crystallographic orientation and orientation spread of individual grains, a new mechanism responsible for the often observed reduction in the rate of coarsening is proposed. Furthermore, multiple modes of grain coarsening are presented.

Results of the effect of crystallographic orientation relationships on the nucleation of the $\gamma$–phase in a model Fe–C–Mn–Ti alloy during heating are described in Chapter 6. For the first time, the $\Psi$–parameter, which represents the effects of the shape of the nucleus and the interfacial energies, is calculated for five different types of $\gamma$–nuclei depending on the number of $\alpha$ neighbours with special orientation relationships.

Grain coarsening in two specially designed alloys with high Nb:C ratios for high temperature applications is studied in Chapter 7. Grain coarsening in these alloys is in complete contrast with ‘normal’ grain coarsening in polycrystalline materials, such as the results shown in Chapter 5.
1.4 Bibliography


1. Introduction


CHAPTER 2

A MULTI−PURPOSE FURNACE FOR IN−SITU STUDIES OF POLYCRYSTALLINE MATERIALS USING SYNCHROTRON RADIATION

Abstract

A multi−purpose furnace designed for studies using synchrotron radiation on polycrystalline materials, namely metals, ceramics and (semi−) crystalline polymers, is presented. The furnace has been designed to carry out Three−Dimensional X−Ray Diffraction (3DXRD) measurements, but can also be used for other types of synchrotron radiation research. The furnace has a very low thermal gradient across the specimen (< 0.2 °C/mm). A thermocouple welded to the specimen is used to accurately determine the temperature. The furnace can be rotated over an angle of 90° in order to determine the crystallographic orientation and the position of each individual grain. It is possible to follow the growth kinetics of all the grains in the illuminated volume of the specimen. The specimen environment can be controlled varying from vacuum (up to 10−5 mbar) to gas or air filled. The maximum temperature of operation is 1500 °C, with the possibility of achieving high heating (up to 20 °C/s) and cooling rates (up to 30 °C/s without quenching...
2. A multi-purpose furnace for in-situ studies of polycrystalline materials using synchrotron radiation

gas). 3D maps of the microstructure of the specimen can be generated at elevated temperatures by positioning a high-resolution detector close to the specimen. An example of a simulation of the heat affected zone during the thermal cycle of a weld in a TRIP steel carried out using the furnace is shown. More examples are shown in Chapters 5, 6, and 7. The unique characteristics of the furnace presented here open the possibility of new fields of research in materials science using synchrotron radiation.

2.1 Introduction

In recent years, high-energy X-ray radiation, available at 3rd generation synchrotron sources such as the European Synchrotron Radiation Facility (ESRF) in Grenoble (France), the Advanced Photon Source (APS) in Argonne (USA), and Spring-8 in Nishi Harima (Japan), has become more and more important for studies in materials science. In particular for polycrystalline materials, X-ray Phase-Contrast Tomography (PCT) [1, 2], Differential Aperture X-ray Microscopy (DAXM) [3, 4], 3-Dimensional X-ray Diffraction Microscopy (3DXRD) [5, 6, 7, 8], and Diffraction Contrast Tomography (DCT) [9, 10, 11] have been used. PCT is a powerful technique to study material systems with an inhomogeneous density distribution, e.g., silicon particles can be visualized in cast aluminium alloys [2], but the crystal orientations cannot be determined. DAXM has nano-metre resolution, but is limited by small specimen volumes and long acquisition times. The 3DXRD technique, developed jointly by scientists at beamline ID11, ESRF and RISØ, Denmark in the 1990s, has shown to be a powerful tool for carrying out in-situ studies in metals. The DCT technique can be considered a variant of 3DXRD.

The 3DXRD technique allows for non-destructive characterization of grains in terms of volume [7, 12], orientations [13, 14] and stresses [14, 15, 16] in bulk microstructures. The experimental setup is rather similar to X-ray tomography, the difference being that, in tomography one probes the attenuation of the direct beam and reconstructs the density of the specimen. However, in 3DXRD, the diffracted signal from different crystalline grains is used to reconstruct the microstructure within the material. In this way, a 3D image of the microstructure can be obtained, even for materials without a density difference, with micrometre resolution. In comparison, Focused Ion Beam (FIB) 3D Electron Back-Scatter Diffraction (EBSD) [17] has a better spatial resolution, but, being a surface technique, is destructive and ex-situ in nature and the volumes that can be investigated are limited. In general, 3DXRD can be used in three modes. In the ‘fast mode’, the characteristics of
each grain (for example volume, position of centre–of–mass and crystallographic orientation) can be obtained with a time resolution of the order of a few minutes. On the other hand, in the ‘slow mode’, full 3D mapping of the grain position, shape and orientation can be carried out, with a mapping precision of $5 \times 5 \times 1 \mu m^3$, but with a worse time resolution of the order of a few hours. In the ‘high–resolution mode’, deformation structures of the material can be investigated by placing the detector at a large distance from the specimen [15]. The 3DXRD setup is shown in Figure 2.1. In order to get all the grains under diffraction a number of times, the specimen is rotated around the vertical axis ($\omega$).

The present chapter describes a furnace specially designed to carry out 3DXRD measurements at temperatures up to 1500 °C, while meeting all the requirements of the setup of the 3DXRD technique. The furnace is suited for studies of polycrystalline materials including metals, ceramics and semi–crystalline polymers. Although the furnace was designed for 3DXRD experiments, it can as well be used for X–ray tomography and DCT in the low temperature mode (see §2.6 for details). In addition, the furnace can also be used for other synchrotron radiation experiments such as High Resolution Powder Diffraction and Small Angle X–ray Scattering (SAXS). The furnace overcomes various shortcomings of the other furnaces currently available for 3DXRD experiments. For example, while operating in the high temperature range, the specimen can be rotated over an angular range of 90°, as compared to a previous furnace reported by Margulies et al. [18], in which rotation is limited to an angle of 9° only, which is not enough to bring all the grains under diffraction sufficient number of times in order to determine the crystallographic orientation of all the grains. Also, the furnace of Margulies et al. [18] cannot be used with high–resolution detectors due to the geometrical constraints arising from the design of such detectors. In comparison, the furnace reported by Bellet et al. [19] has the advantage that, being a tomography furnace, it can be rotated over an angle of 360°. However, it suffers from the disadvantage that the maximum temperature that can be reached is 1030 °C and, because the specimen is heated directionally from the bottom, has a considerable thermal gradient across the specimen. Furthermore, the high temperature stability of the furnace of Bellet et al. [19] is not good enough for full 3D mapping using the high resolution detector at high temperatures and there is no possibility to accurately determine the specimen temperature by welding a thermocouple to it. There are also other furnaces available for high temperature synchrotron experiments, e.g., the furnace reported by Brokmeier et al. [20], but they are not suited for 3DXRD measurements due to space and other constraints.
2. A multi-purpose furnace for in-situ studies of polycrystalline materials using synchrotron radiation

Figure 2.1: Schematic of the 3DXRD setup. Shown in the figure are the incident beam direction, the location of the specimen and furnace around it, and the 2D detector to record diffraction images. During the experiment, the specimen is rotated around the vertical axis over an angle \( \omega \) in order to bring all the grains into diffraction multiple times.
2.2 Design Requirements

§2.2 describes the challenges that arise from the specific requirements of the 3DXRD technique, while details of the furnace design are covered in §2.3 §2.4 covers the characteristics and performance of the furnace. An example of an experiment carried out using the furnace is presented in §2.5.

2.2 Design Requirements

The requirements of the furnace, which were kept in mind during its design and are in accordance to the 3DXRD technique, are listed as follows: Firstly, the furnace should permit rotation of the specimen around the vertical axis ($\omega$) in order to be able to map all grains in the specimen and, at the same time allowing a high-resolution (e.g., Quantix [21]) detector to be placed at a small distance from the centre of the specimen (of the order of 8 mm). For the latter, the vertical distance between the beam position and top of the furnace also needs to be kept low (of the order of 14 mm), due to space constraints dictated by the geometry of the high-resolution detectors. The X-ray absorption of the furnace chamber needs to be low enough in order not to interfere with the measurements. It should be possible to achieve high heating (up to 10 °C/s) and cooling (up to 30 °C/s) rates with accurate temperature measurement by welding at least one thermocouple to the metallic specimen. This is important to simulate in situ heat treatments of metals and ceramics, for example, thermal cycles during welding in steels [22]. The temperature-time profile should be controlled accurately in order to simulate complex heat treatments that are required for the production of e.g., modern TRansformation Induced Plasticity (TRIP) steels. Heating of the specimen (metallic or ceramic) should be uniform to reduce thermal gradients within the specimen (< 1 °C over the beam), needed to ensure that the measured temperature with the thermocouple is the same as the temperature at the position of the synchrotron beam. This is important because many metallurgical processes like diffusion of atoms depend exponentially on temperature. Environment control inside the furnace chamber should allow for working in a controlled atmosphere or under vacuum. Among others, this is important for steel research, because the carbon atoms can rapidly diffuse out of the steel in the presence of an oxygen-containing atmosphere, which would have a large effect on e.g. the transition temperature of the austenite-to-ferrite phase transformation in steel. The furnace should be able to heat the specimen up to 1500 °C while keeping the temperature in front of the high-resolution detector lower than 40 °C to prevent damage to the detector. The furnace should be able to operate at high temperatures (> 800 °C) continuously for
2. A multi-purpose furnace for in-situ studies of polycrystalline materials using synchrotron radiation

5 days, the typical duration of a 3DXRD beam time. The furnace design should also allow for thermal expansion of the specimen without deformation, while making sure that the specimen stands vertically straight. A deformation free specimen is very important to study, e.g., phase transformation kinetics in steels, where small deformations can lead to considerable changes in the nucleation and growth rates [23].

2.3 Furnace design

Although it was envisioned to design a furnace in which the beam could access the specimen over an angular range of 360°, the required temperature of 1500 °C did not allow for a design with full rotation of the specimen. The furnace has been designed for a free rotation of the specimen over 90° on the frontside and 90° on the backside and the openings of the heating element dictate the maximum rotation angle. The asymmetric shape of the furnace results from the requirement of placing a high-resolution detector at a small distance from the specimen, while allowing for rotation of the specimen. The specimen is heated by radiation (from the heating coil) and convection (by the gas present in the specimen chamber). The schematic design and a real picture of the furnace are shown in Figure 2.2. The following subsections describe the design of the different parts in detail.

2.3.1 Furnace body

The furnace base and top are made of brass (Cu—64 wt%, Zn—36 wt%) to have a good thermal conductivity. The furnace weighs around 5 kg, excluding the weight of the vacuum assembly. The total height of the furnace is approximately 15 cm. The furnace is water cooled by the means of two channels, one in the base and one in the top. This assists in keeping the temperature variations of the furnace assembly low, thus providing good vertical stability of the specimen during experiments, which is important to ensure that the same specimen volume is measured during heating and cooling of the specimen. The thermal expansion of the specimen itself can be corrected for (see §2.3.3). Two vacuum feedthroughs are used to connect the thermocouples, one thermocouple through the base, on which the specimen is positioned and one thermocouple through the top, which is welded to the top of the specimen. The heating element is connected to a power supply also through the bottom feedthrough. A channel through the top can be used as an inlet for gas, regulated by a Bronkhorst digital EL–FLOW F—201CV™ electronic mass flow controller. The furnace base has a channel connected to a pressure gauge, a vacuum pump and
2.3. Furnace design

Figure 2.2: Schematics and a real image of the 3DXRD furnace. Different views are shown in (a), (b) and (c) and the real furnace is shown in (d).
2. A multi-purpose furnace for in-situ studies of polycrystalline materials using synchrotron radiation

![Diagram of furnace components]

**Figure 2.3:** Cut-out view of the 3DXRD furnace. Difference parts of the furnace are indicated. One thermocouple is spot welded on the top of the specimen.

A gas outlet. The furnace base and the top are connected by two supports. Cut-out views of the furnace base, supports and top are shown in Figure 2.3. Two specially designed leader pins in each support assist in positioning the top at its designed place. In order to change the specimen, the furnace top can be removed with the help of two counter screws. A high precision translation table with micrometre screws is used to position the furnace in the centre of rotation. This is important for tomographic measurements from which the 3D structure of the specimen is reconstructed.
2.3. Furnace design

Figure 2.4: Cut-out view of the specimen chamber. The setup with two quartz tubes is shown. The X-ray beam direction and location of specimen is indicated. For changing the specimen, furnace top is removed and the specimen is dropped onto the bottom thermocouple. Geometry of the specimen can be seen with the step due to the change in diameter visible.

2.3.2 Specimen chamber

The specimen chamber, shown in Figure 2.4, consists of a region covered by a high purity (99.995%) quartz tube (1 mm thick to minimize background). To achieve optimum sealing of the specimen chamber, polymer O-rings are used between the quartz tube and the furnace base and top. Since the O-rings are less than 6 mm away from the heating element heated to temperatures greater than 1500 °C, the O-rings also get heated to high temperatures. To ensure proper service, Kalrez® O-rings are used, which can withstand temperatures up to 317 °C. Helium present in the specimen chamber heats the specimen very effectively by convection.
2. A multi-purpose furnace for in-situ studies of polycrystalline materials using synchrotron radiation

However, it also heats up the O-rings to high temperatures. Hence, in the case of long annealing times (> 5 hours) at high temperatures (> 800 °C), a different setup has been designed. An additional quartz tube with two O-rings is placed on the inside of the original quartz tube. The O-rings for this quartz tube are even closer to the high temperatures and start to degrade quite soon. However, at the same time, they act as a barrier for helium access to the outer O-rings and thus keep the temperature of the outer O-rings low, resulting in longer vacuum stability. The construction with the double quartz window simultaneously acts as a heat shield to keep the temperature just outside the furnace low where an expensive high-resolution detector is positioned. The background signal during synchrotron radiation measurements from the quartz tubes is low for X-ray energies usually used for studies of metals, i.e. 50 keV or more.

2.3.2.1 Atmosphere control

Before heating up, the specimen chamber can be alternatingly purged with helium and kept under vacuum to get rid of any air remaining in the specimen chamber. The heat shield, made of pure tantalum or titanium, has two windows for the incoming and transmitted/diffracted beams and is put around the specimen and the heating coil in order to minimize heat losses to the surroundings. It simultaneously acts as a getter at high temperatures for any oxygen left behind. In addition, a small titanium ring is placed on the top of the heating element for the same purpose. The furnace can be operated under different specimen environments ranging from low pressure (up to 10^{-5} mbar) to controlled gases at desired pressure and also in air. The sealing of the specimen chamber has been checked using a helium leak detector before, during and after a heat treatment (isothermal annealing at 1100 °C for 3 hours) to check the degradation of the O-rings. The rate of helium leakage was found to be lower than 10^{-9} mbar l/s. No change in the leakage rate was detected after the heat treatment, showing minimal or no damage to the outer O-rings.

2.3.3 Heating element and specimen holder

Although heating can be carried out by various methods such as induction heating, laser heating etc., the special requirements (a low thermal gradient and heating of a ceramic specimen etc.) of the furnace allowed for resistance heating only. In order to minimize the thermal gradients in the specimen, heating is done by passing DC current through a coil (Pt−10% Rh, φ = 0.25 mm) wound on a ceramic
2.3. Furnace design

carrier (Al\textsubscript{2}O\textsubscript{3} tube, inner diameter $\phi = 2$ mm) directly around the specimen (Figure 2.4). The Pt–Rh wire is chemically inert and can be heated to temperatures up to 1750 °C. The specimen is made out of a cylinder. The diameter changes three times abruptly over the length of the specimen (see Figure 2.4). At the top and the bottom of the specimen, the diameter is the largest and just fits into the cylindrical ceramic carrier in order to position the specimen vertically straight and at the same time allow for free thermal expansion of the specimen in order to avoid any deformation of the specimen. At the location of the smallest diameter ($\phi = 1$ mm), the 3DXRD measurements are performed. The intermediate diameter is used to serve as a reference point, which can be found with the synchrotron beam by monitoring the attenuation of the primary beam, which is higher in the thicker part of the specimen. Another method is to record the image of the specimen using the high-resolution detector. From the step edge, the specimen is moved with respect to the beam to the measurement location. In this way, the location where the synchrotron beam interacts with the specimen is exactly known. This gives the opportunity to perform ex–situ electron microscopy and EBSD measurements after the synchrotron measurements at exactly the same location where the synchrotron measurements were performed.

The specimen is lowered from the top on to the bottom thermocouple. S–type thermocouples ($\phi = 0.15$ mm) are used for temperature measurements. This was chosen for two reasons: (i) S–type thermocouples are the most accurate at high temperatures and; (ii) the thin thermocouple wires help in minimizing the time lag for temperature readout and do not act as a heat sink. The inner diameter of the ceramic tube is chosen to allow for expansion of the specimen at higher temperatures. For minimizing heat loss to the surroundings, the volume of the specimen is kept small (8.5 mm\textsuperscript{3}), which allows for a low power requirement and also high heating and cooling rates. Small specimen volumes are sufficient for many investigations, because many of the microstructural changes in polycrystalline materials are in the order a few nanometres up to a millimetre.

2.3.4 Furnace control

Furnace control is achieved by using Eurotherm\textsuperscript{©} 3504 controller connected to a computer. Process modelling can be achieved on the controller or via the iTools\textsuperscript{®} program. For temperature control, either both or one of the two thermocouples at bottom and top of the specimen can be used. However, since the top thermocouple is welded directly on top of the specimen, it serves as the most accurate means
of temperature measurement and control. The heat treatments and the gas flow can be programmed in the software. Real time recording of different parameters such as the temperature of the top and the bottom of the specimen, the gas flow conditions used, and the programmed parameters etc. can be carried out.

### 2.4 Furnace characteristics and performance

Due to the small size of the specimen, a very wide range of heating (up to 20 °C/s) / cooling rates can be achieved. Although quenching by helium can also be carried out, in most cases, the specimen can cool down at a rate of 30 °C/s just by switching off the power supply, with higher cooling rates possible by using a helium flow. Only 35 W of power is required to heat the specimen up to 1000 °C, with the limit for maximum allowable power up to 80 W. The furnace can safely achieve temperatures up to 1500 °C. This has been tested by melting a steel specimen, which had a melting point above 1500 °C. The use of a PID controller like Eurotherm® 3504 allows for accurate temperature control and stabilization. For the temperature constraint arising from the close proximity of the high-resolution detector with the specimen at 1000 °C, the temperature at a distance of 10 mm from centre of the specimen reaches around 58 °C with only the outer quartz tube present. This is higher than the allowable limit of 40 °C for the high-resolution detector. This temperature can be brought down to around 26 °C by using a cooling fan outside the furnace. Furthermore, in order to reduce the heating by radiation, a reflective aluminium foil, 0.8 μm in thickness, can be placed between the two quartz tubes. This is important when operating at temperatures above 1200 °C due to the increased radiation. The temperature gradient in the specimen, measured during a thermal cycle of continuous heating from room temperature to 1000 °C in 2 min, holding isothermally at 1000 °C for 10 min and continuous cooling to room temperature in 5 min, was found to be less than 0.5 °C between top and middle of the specimen.

### 2.5 Experiments

3DXRD experiments on the furnace were carried out in December 2008, July 2009, July 2010 and December 2010 at beamline ID11 at ESRF. Figure 2.5 shows the furnace installed at the beamline. The setup shown combines the use of both a high-resolution (Quantix [21]) and a medium-resolution (FReLoN [24]) detector simultaneously, in which the high-resolution detector is partially transparent. Quantix also has a slit to allow the primary X-ray beam through. Figures 2.6(a, b)
2.5. Experiments

Figure 2.5: Photograph of the 3DXRD furnace installed at beam line ID11 at the ESRF. The furnace is mounted on a rotation and translation table for positioning in the beam. The location of the high resolution (Quantix) and the medium resolution (FReLoN) detectors is indicated. The high resolution Quantix detector has a slit for the primary beam and is semi-transparent.

The high-resolution images show two examples of diffraction images recorded simultaneously using the Quantix and the FReLoN detectors, respectively. The specimen (steel alloy of composition Fe–1 wt% Mn) was at 780 °C at the time of the measurement, with the Quantix a distance of 10 mm away from the centre of the specimen and the FReLoN a distance of 225 mm away. With cooling achieved using a fan, the measured temperature in front of the Quantix detector was 24 °C (2 °C above ambient temperature). A beam size of 1200×300 μm² was used. The X-ray energy was calibrated to 78.395 keV using the Laue–Laue setup and the specimen was rotated over an angle of 0.3° during each exposure. The exposure time for FReLoN and Quantix detectors was equal to 0.2 s and 5 s, respectively. Due to the close position of the Quantix detector with respect to the specimen, the position of the grains in the specimen strongly influence the position of the diffraction spots on the high-resolution detector, as shown in Figure 2.5.
2. A multi-purpose furnace for in-situ studies of polycrystalline materials using synchrotron radiation

Figure 2.6: Examples of diffraction images recorded from (a) high resolution Quantix detector; (b) medium resolution FReLoN detector, simultaneously.

2.6 (a) [25]. In the case of the FReLoN detector, the position of the diffraction spots is influenced to a much smaller extent by the position of the diffracting grains in the specimen because the FReLoN detector is positioned at a distance of typically 250 mm away from the specimen. This is the reason why diffraction rings cannot be observed in Figure 2.6 (a), but can be observed in Figure 2.6 (b). More detailed treatment of the experiments with the FReLoN detector is given in Chapters 3 and 4.

Figure 2.7 shows a simulation of the thermal cycle during welding carried out on a TRIP steel specimen (composition, wt%: 0.19% C, 1.63% Mn, 1.1% Al and the rest Fe) and also examples of the diffraction images recorded using the FReLoN detector at the different stages during the heat treatment. The specimen was heated from the room temperature (Figure 2.7 A) at a rate of 15 °C/s to 1000 °C (Figure 2.7 B), held isothermally at 1000 °C for 60 s (Figure 2.7 C and D) and quenched (Figure 2.7 E) at an average rate of 15 °C/s to room temperature (Figure 2.7 F). The maximum cooling rate was 36 °C/s from 1000 °C to 600 °C. At lower temperatures, the cooling rate was reduced to simulate welding conditions [22]. Diffraction images were recorded every 0.3 seconds.
Figure 2.7: Example of diffraction images recorded during welding thermal cycle on a TRIP steel. 

A—diffraction image recorded from the initial TRIP microstructure. 
B—diffraction image recorded during heating. 
C—diffraction image recorded at the beginning of isothermal holding. 
D—diffraction image recorded at the end of isothermal holding. 
E—diffraction image recorded during quenching. 
F—diffraction image of the final microstructure at room temperature. Darker regions represent pixels with positive intensity. Presence of both austenite and ferrite diffraction spots can be seen in the diffraction images.
2. A multi-purpose furnace for in-situ studies of polycrystalline materials using synchrotron radiation

During the experiments, the stability of the setup was checked by carrying out various experiments on a single specimen for 32 hours. A specimen was kept at 900 °C for a total of 12 hours and was heated up and cooled down from and to 600 °C four times. At the end of the experiments, no oxidation was observed on the specimens and the specimen chamber was still leak tight in each case. This shows that the furnace is ideal for long experiments without the need of changing the specimen while decreasing the beam time wasted for changing specimens.

2.6 Future developments

In future, the furnace can be modified to achieve a field of view of 360° (except for a shadow of the heating coil), by removing the ceramic carrier and the heating coil wound on it (see Figure 2.4 for details). These will be replaced by only a heating coil of Pt–10% Rh, the top and its supports will be removed and the furnace chamber will be covered with closed quartz. This setup would be very useful for techniques such as DCT, which require a full 360° rotation around the specimen axis. However, due to the reduced efficiency of heating from the wire, the maximum specimen temperature in this setup that can be reached would be limited to around 900 °C due to absence of a ceramic carrier for heat transfer to the specimen.

In addition, the furnace chamber has been modified to fit the requirements for SAXS experiments. In the setup described here, while operating at low X-ray energies (< 20 keV), absorption and scattering signal from the quartz tubes can become significant. In such cases, the quartz tube is replaced by a specially designed steel enclosure with two slits for the incident beam and scattered signal. The two slits are covered with Mica foils (to ensure minimum absorption or scattering signal from the foils), held in place using a plate—on—plate design and sealed using high—temperature O—rings. However, the maximum specimen temperature in this setup is limited by the limited high—temperature stability of the Mica foils.

2.7 Conclusions

A furnace designed for carrying out synchrotron radiation experiments for polycrystalline materials research is presented. The furnace combines various requirements of materials science research, such as fast heating (20 °C/s) and cooling rates (30 °C/s), high operating temperatures (1500 °C), low temperature gradients across the specimen (< 1 °C), accurate temperature control and control of the specimen
environment (vacuum up to $10^{-5}$ mbar or gas filled), with the requirements of synchrotron radiation techniques (for example 3DXRD, SAXS and PCT), such as rotation of the specimen over a wide angular range ($90^\circ$), space and temperature constraints from the detectors and low X-ray absorption of the furnace chamber. With the help of examples, the various strengths of the furnace are illustrated. A number of demonstrative examples of the furnace in use for metals research are shown in Chapters 5, 6 and 7. Its unique characteristics open up new fields of research in materials science such as studies of the kinetics of phase transformations and the simulation of welding conditions in metals. Although designed for metals research using the 3DXRD technique, the furnace is expected to prove to be an invaluable tool for ceramics research and be applied to other synchrotron radiation techniques as well.

2.8 Bibliography


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2.8. Bibliography


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CHAPTER 3

PREPROCESSING OF 3DXRD DIFFRACTION DATA

Abstract

A procedure for the pre-processing of data acquired using 3-Dimensional X-Ray Diffraction (3DXRD) is presented. The procedure deals with the pre-processing of the data for input in the algorithms presented in Chapter 4 for the determination of grain characteristics. An algorithm is presented for accurate identification of overlapping diffraction peaks from X-ray diffraction images, which has been a long-standing issue for experiments of this type. The algorithm works in two stages, namely, identification of overlapping peaks by using a seeded-watershed algorithm and then fitting the peaks with a pseudo-Voigt shape function to yield accurate centre-of-mass position and integrated intensity of the peaks. Regions consisting of up to six overlapping peaks can be successfully fit. Two simulations are used to verify the results of the algorithms. An example of the processing of diffraction images acquired in a 3DXRD experiment with a specimen consisting of more than 1600 grains is shown. Furthermore, a procedure for the determination of the parameters of the experimental setup (global parameters) without the need of a calibration specimen is described and validated using simulations. This is immensely beneficial for simplifying the experiments and the subsequent data analysis.
3. Pre-processing of 3DXRD diffraction data

3.1 Introduction

In the last decade, a number of techniques have been developed for non-destructive characterization of three-dimensional (3D) microstructures of polycrystalline materials using high energy X-ray diffraction available at 3rd generation synchrotron sources. A few examples include Differential Aperture X-ray Microscopy, DAXM [1], 3D X-Ray Diffraction microscopy, 3DXRD [2,3], and Diffraction Contrast Tomography, DCT [4]. DAXM has nanometre resolution, but requires time-consuming acquisition strategies and is limited to relatively small volumes. 3DXRD and DCT, which can be considered a variant of 3DXRD, allow for the simultaneous characterization of volume, crystallographic orientation and stresses in bulk microstructures with micrometre resolution. These two techniques have been used to investigate changes in polycrystalline materials at the microstructural level and have led to better understanding of the complex processes involved during heat treatments and deformation of materials [2,5,6,7,8]. In general, 3DXRD can be used in three modes. In the ‘fast-mode’, the average characteristics of each grain (that is, volume, centre-of-mass position, crystallographic orientation and average strain state) can be obtained with a time resolution of the order of a few minutes. In the ‘slow-mode’, grain shape, position and crystallographic orientation can be mapped with a time resolution of the order of a few hours. In the ‘high-resolution mode’, crystallographic orientation of and strains within individual crystals can be mapped in reciprocal space, again with a time resolution of the order of a few hours. A full overview of the technique can be found elsewhere [9].

The present chapter deals with the analysis of data acquired using ‘fast-mode’ 3DXRD. In this technique, if the number of grains in the volume illuminated by the X-ray beam is limited, the number of grains that satisfy the Bragg diffraction condition for an orientation of the specimen is also limited, leading to individual diffraction spots from individual grains, which can then be used to determine the characteristics of the grains. Thus, the technique is intermediate between single crystal diffraction and powder diffraction. As the number of grains in the illuminated volume increases (or in the case of textured/deformed materials), diffraction spots from different grains overlap. This problem has been highlighted as a long-standing limitation of the 3DXRD type of experiments a number of times in References [9,10,11,12,13,14]. A strategy widely used to overcome this problem has been to reduce the illuminated volume and scan multiple volumes (so-called ‘layers’) in the specimen, see, e.g, Oddershede et al. [11]. However, this results in worse time resolution during the acquisition of data as compared to a
3.2 3DXRD technique

The setup of the 3DXRD technique operating in ‘fast—mode’ is schematically shown in Figure 3.1(a). A collimated and monochromatic beam with a rectangular cross-section\(^1\) is incident on the specimen. The specimen, of a known structure, is placed on the top of a rotation setup comprising of an \(\omega\) rotation stage (\(\omega\) is the rotation around an axis perpendicular to the X-ray beam) and multiple \(x\), \(y\) and \(z\) translation tables for alignment. The specimen can also be placed in a special environment for carrying out in—situ studies (e.g. the multipurpose furnace presented in Chapter 2). In any orientation of the specimen, the grains that satisfy the Bragg diffraction condition will generate a diffracted beam leading to a signal on the two—dimensional detector. In order to get all the grains in the illuminated volume under diffraction a number of times, the specimen is rotated around the \(\omega\)—axis. Since real materials consist of imperfect grains having variations in the orientation (so—called mosaicity), the specimen is rotated by an angle \(\Delta \omega\) during each exposure to bring all parts of the grains in diffraction.\(^2\)

In the ‘fast—mode’ 3DXRD, diffraction images are acquired by using only the far—field detectors with a pixel size of the order of 50 \(\mu\)m placed relatively far from the specimen (\(\sim 20—50\) cm), due to which the diffraction spots appear at the intersection of the Debye—Scherrer cones (with opening angle \(4\theta\)) and the detector plane, so called diffraction rings. In case the mosaicity of a grain is sufficiently large, or \(\Delta \omega\) sufficiently low (described in §3.3.3), diffraction spots are observed in multiple diffraction images, with spots in each image being characterized as diffraction peaks. For undeformed grains (or grains with homogeneous intra—grain

---

\(^1\)The shape of the beam is usually of the following form: (a) pencil (both horizontal and vertical dimensions of the beam are smaller than the average grain size), (b) slice (either horizontal or vertical dimension of the beam is increased to illuminate multiple grains only in 1D) and, (c) rectangular (both vertical and horizontal dimensions of the beam are larger than the average grain size to fully illuminate multiple grains).

\(^2\)Rotation over \(\Delta \omega\) enables recording diffraction spots from ‘near-perfect’ grains as well.
3. Pre-processing of 3DXRD diffraction data

Figure 3.1: Overview of the 3DXRD technique. (a) Schematic of the ‘fast-mode’ 3DXRD setup with the far-field detector. The dimensions are not to scale. The angles 2θ, ω and η are defined. (b, c) Definition of detector tilts. (b) Schematic view of the diffraction ring as observed on the tilted detector and as it should appear on a perfect detector. (c) 2D view of the schematic shown in (b).
3.3 Characterization of peaks

In the case of diffraction images containing no overlap, a direct approach can be adopted. A single thresholding operation on the corrected diffraction images yields the position of all connected pixels in an image, each set of connected pixels being a diffraction peak. Various characteristics of the diffraction peaks such as integrated intensity, centre-of-mass position etc. can then be calculated [11, 13]. For non-overlapping peaks, Edmiston et al. [13] use a 3D Gaussian function for fitting the peak shape after coordinatizing the peak position in $(2\theta, \eta, \omega)$ from $(y, z, \omega)$. However, if overlapping peaks are present, this procedure leads to erroneous results because each set of overlapping peaks is counted as one and thus the calculated centre-of-mass position and the integrated intensity of the peaks are

---

3Wedge is defined as the deviation of the axis of rotation from the ideal rotation axis orthogonal to the x-ray beam.
wrong. This can be avoided by combining the results of multiple thresholds,\(^4\) which can resolve the overlapping peaks, but the integrated intensity of the peaks is still wrong, and in the cases with strong overlap, so is the centre—of—mass position of the peaks. In order to overcome such problems, the shape of the diffraction peaks can be fit using an ideal shape (in 2D or 3D) to obtain refined characteristics of the diffraction peaks. To this end, the program DIGIgrain \(^{15}\) employs a 3D connectivity peak search to characterize overlapping diffraction peaks. In this section, a complementary technique is presented, which employs a 2D peak fitting routine in order to efficiently resolve and characterize overlapping peaks.

The diffraction images acquired in 3DXRD usually consist of a large number of pixels with background intensity interspersed with a considerably lesser number of pixels with signal (intensity higher than the background) from the diffracting grains on the diffraction rings. For diffraction data with peak overlap, the determination of the peak characteristics by fitting the diffraction image as a whole with multiple diffraction peaks can be computationally very intensive and un—wise because: (i) a significant number of pixels (background) are not of interest and thus need not be processed; (ii) the parameters (width, height etc.) defining the shape of each peak to be used during fitting can vary significantly depending on the size of the diffracting grains, orientation spread within the grains and the position of the diffraction spots and; (iii) depending on the number of peaks in the diffraction image, the number of parameters to fit can be very large. In the methodology presented here, these issues are avoided as follows: (i) the background pixels in the image are removed by applying a threshold to the diffraction image; (ii) each set of interconnected pixels with intensity above the threshold is considered separately during fitting as a set of overlapping peaks (a considerably smaller set compared to all the peaks present in the diffraction image) and; (iii) guesses for the parameters to be fit are obtained by using the information about the connected pixels. The procedure for the determination of the characteristics of the peaks is then divided into three parts:

(i) A peak searching algorithm to carry out the thresholding operation, to determine the number of peaks in each set of connected pixels using the number of maxima and to determine approximate characteristics of the peaks (integrated intensity and centre—of—mass position) using a seeded—watershed operation \(^{16}\).

\(^{4}\)The algorithm for peak searching using multiple thresholds can be provided upon request. Alternatively, an implementation of peak searching using multiple thresholds is available in the Fable package at \url{http://fable.svn.sourceforge.net/viewvc/fable/ImageD11/trunk/scripts/merge_flt.py?view=log}.
3.3. Characterization of peaks

(ii) A peak fitting routine to refine the peak characteristics by fitting the peak shape with a symmetric 2D function.

(iii) Merge the overlapping peaks in successive images ($\omega$) to obtain the position coordinates in $(y, z$ and $\omega$) for un–deformed samples or in $(2\theta, \eta$ and $\omega$) for deformed samples.

3.3.1 Peak searching

Each pixel in the diffraction images is corrected for background (a combination of the dark current of the detector and the background from the specimen), flood of the detector\(^5\) and beam current as follows:

$$I_{\text{corr}} = I_{\text{raw}} - I_{\text{BG}} - \frac{I_{\text{flood}}}{BC_{\text{ref}}} BC_{\text{img}}$$ \hspace{1cm} (3.1)

where, $I_{\text{corr}}$ is the corrected intensity, $I_{\text{raw}}$ is the recorded intensity, $I_{\text{BG}}$ is the background intensity and $I_{\text{flood}}$ is the correction for flood, which is scaled with respect to 1: a value less than 1 means pixels are less active than normal (can be arbitrarily defined as either the average pixel response or the median pixel response) and a value greater than 1 means pixels are more active than normal. As described in Reference \([17]\), the diffracted intensity from a grain is directly proportional to the incident intensity, which, in turn, is directly proportional to the number of electrons in the storage ring of the synchrotron (defined by the beam current). During an experiment, the beam current decreases gradually due to the loss of electrons in the storage ring and more electrons are injected at regular intervals to compensate for this decrease.\(^6\) Due to this, the incident intensity is not constant during the experiment and is corrected for by scaling to a reference beam current ($BC_{\text{ref}}$) in Equation 3.1 where $BC_{\text{img}}$ is the beam current during acquisition of the image. Instead of the beam current, the incident intensity can also be corrected by using a semi–transparent diode placed before the sample in the X–ray beam, which gives a reading directly proportional to the incident intensity.

A thresholding operation is then carried out during which the intensity of all the pixels with intensity below the threshold is set as 0. The interconnected pixels in the image are then identified as ‘regions’. The user can choose the type of

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\(^5\)Flood is defined as the heterogeneity in pixel response to photons

\(^6\)This injection of electrons can either be continuous (e.g. at the Synchrotron Soleil in Paris), or every few hours (e.g. at the ESRF in Grenoble).
connectivity to be used, 4—or 8—connected neighbourhood. In each region, the total number of pixels with intensity higher than the neighbouring pixels (local maxima) determines the number of peaks present. If only a single maximum is detected in the region, the characteristics (intensity weighted centre—of—mass, integrated intensity, maximum intensity and number of pixels) of the single peak in the region are calculated and stored for fitting.

If more than one maximum is found, the intensities in the region are first inverted (multiplied with $-1$). The pixels in the inverted region outside the pixels belonging to the peaks are set to a value equal to $-\infty$. The pixels in the inverted region corresponding to the local minima (or local maxima in the original image) are also set to a value equal to $-\infty$. This operation is important to ensure proper result of the watershed algorithm, with all the pixels with intensity equal to $-\infty$ being the seeds. Watershed \[16\] is then carried out in the region using the inverted modified image. For this, the function \textit{watershed} in MATLAB\textsuperscript{®} is used. The output of watershed is a list containing the pixels belonging to each peak. The integrated intensity of each peak is calculated by summing the intensity of all the pixels belonging to each peak. The integrated intensity of each peak is calculated by summing the intensity of all the pixels belonging to each peak.

The initial guess of the centre—of—mass of the peaks to be used subsequently for fitting can be calculated in three different ways. The first approach is to skip watershed and just take the position of the local maxima as the centre—of—mass of the peaks and continue to fit. Second, the intensity weighted centre—of—mass of the peaks can be calculated simply by using the pixels belonging to each peak obtained from watershed. However, this can result in discrepancies due to the asymmetric shape of the result of watershed. In the third approach (improved watershed), the pixels belonging to the border of a peak are determined. Then, the maximum intensity of these border pixels is calculated. A thresholding operation using a threshold higher than this maximum intensity is carried out on the pixels belonging to the peak. This results in a more symmetric shape of the peak, which is used to calculate the intensity weighted centre—of—mass of the peak. Here, improved watershed is used for calculating the centre—of—mass of the diffraction peaks.

### 3.3.2 Peak fitting

The program for fitting requires input from peak searching and can successfully fit up to six overlapping peaks. If the number of overlapping peaks is more than six, then the first six peaks in decreasing order of maximum intensity are fit, the rest are assigned the characteristics obtained from peak searching. The algorithm
works in two stages, fitting and merging peaks in $\omega$. Outputs of the program are
two files, one file containing the refined parameters of the peaks which were fit
successfully and another file containing the peaks which were not fit successfully.
In the present framework, the results of peak searching are only used as initializing
values for fitting and thus the accuracy of these values is not paramount. However,
in case the results of fitting are not satisfactory, or in the case of smallest peaks
(based on the maximum intensity) in the regions with more than six overlapping
peaks, the results of peak searching are used and thus finding the best estimate is
important.

### 3.3.2.1 Minimization

The algorithm is designed to fit peaks using a 2D pseudo–Voigt function, although
a Gaussian or a Lorentzian function can also be used. The function minimized in
the fitting program is:

\[
\sum \left( I - \left( I_0 + \sum_n A_n (\mu_n L_n + (1 - \mu_n) G_n) \right) \right)^2
\]  
(3.2)

\[i.e.\] the sum of the squared difference between the recorded intensity in the dif-
fraction image and the intensity according to the parameters of the peaks with
the 2D pseudo–Voigt profile. $I$ is the recorded intensity of the $y_i z_j^{th}$ pixel on the
detector. $L_n$ and $G_n$ are the Lorentzian and the Gaussian contributions per peak, respectively, given by:

\[
L_n = \frac{1}{\left(1 + \left( \frac{y_i - y_c^n}{w_1^n} \right)^2 \right) \left(1 + \left( \frac{z_j - z_c^n}{w_2^n} \right)^2 \right)}
\]  
(3.3)

and

\[
G_n = \exp \left( -0.5 \left( \frac{y_i - y_c^n}{w_1^n} \right)^2 - 0.5 \left( \frac{z_j - z_c^n}{w_2^n} \right)^2 \right)
\]  
(3.4)

The parameters which are refined are the background intensity ($I_0$) and, per
peak, the maximum intensity ($A$), the Lorentz fraction ($\mu$), the coordinate position

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7The criteria for determining a successful fit are described later in §3.3.2.2
of the centre \((y_c^n, z_c^n)\) and the width in \(y\) and \(z\) direction \((w_1^n, w_2^n)\) of the \(n\)-th peak in the search region.

In the case of deformed grains, since the spread of the diffraction peaks is along the \(2\theta\) and \(\eta\) directions, the position coordinates of the peaks are converted from \((y,z)\) to \((2\theta,\eta)\) during watershed and in Equation 3.2 during fitting. However, for un-deformed grains, \((y,z)\) coordinates are used during watershed and in Equation 3.2 due to lower computational requirements using \((y,z)\) coordinates as compared to \((2\theta,\eta)\) coordinates.

### 3.3.2.2 Implementation and workflow

The algorithm has been implemented in MATLAB®. The minimization of Equation 3.2 is carried out using the function \textit{fminunc}\(^8\) inbuilt in MATLAB®. Although \textit{fminunc} is a local minimization routine, it has been observed that initial guesses of the parameters obtained from peak searching are good starting points to find the global minimum.

For each diffraction image, the algorithm first inputs the list of search regions in that diffraction image and the parameters of the search regions. Then, for each search region (a set of interconnected pixels), including the regions containing only one peak, the program inputs the corrected (for background, flood and beam current) intensity of each pixel in the search region from the diffraction image. The fitting routine is then called to minimize the function in Equation 3.2 and refine the six parameters per peak and the background intensity using the initial guesses obtained from peak searching. Integrated intensity of a peak is calculated as the area under a pseudo-Voigt peak with the fit parameters for the peak. The results of fitting are accepted based on the criteria given below; this is also shown schematically in Figure 3.2.

\textit{Maximum intensity.} Maximum intensity of the fit peaks \((A_n)\) should be within the minimum and the maximum limits defined as follows: the minimum limit is dictated by the threshold, which was used during peak searching. The maximum limit is determined by the upper limit of the detector. In the case of detector overflow,\(^9\) diffraction peaks no longer have regular shapes, and the results of fitting

\(^{8}\)http://www.mathworks.com/help/toolbox/optim/ug/fminunc.html

\(^{9}\)Detector overflow is the case when more photons are incident on the detector pixels than the pixels can handle. This results in non-linear response of the pixels and thus the intensity values recorded cannot be used correctly any more.
3.3. Characterization of peaks

Figure 3.2: Flow diagram of the procedure for filtering the fitting results. The integrated intensity calculated using the results of fitting is matched with the integrated intensity obtained from peak searching.
are thus rejected. All the results that pass this criterion are passed on to the next step.

**Overlapping peaks.** If overlapping peaks were detected in the search region, the following criteria\(^1^0\) are judged sequentially:

1. The centre-of-mass of each peak should lie in the search region and within a distance of 1.5 pixels (or the corresponding distance in 2\(\theta\) and \(\eta\) for deformed grains) from the position of the maximum intensity of the peak.

2. The difference between the total integrated intensity of all the peaks in the search region and the total intensity in the search region should be less than 10\% of the total intensity.

**Non-overlapping peaks.** In the case that peak searching detected only one peak in the search region, the following criteria\(^8\) are used:

1. The centre-of-mass of the peak calculated from fitting should be within a distance of 0.5 pixels (or the corresponding distance in 2\(\theta\) and \(\eta\) for deformed grains) from the centre-of-mass calculated from peak searching.

2. The difference between the total integrated intensity of the peak and the total intensity in the search region should be less than 10\% of the total intensity.

For the non-overlapping peaks that fail any of the two criteria, the procedure described next is carried out.

**Searching for ’hidden’ peaks.** In case peak searching detected only one peak in the search region and results of the fit failed the screening criteria, the following two cases are possible:

1. There are two peaks in the search region with only one maximum, the second one being buried in the ‘shoulder’ of the first peak. In such cases, a derivative search is carried out in 8 equally spaced directions radially outwards from the maximum intensity in the search region. This procedure works only for search regions big enough to yield two or more distinct minima in the derivative. If the derivative search yields two minima of the derivative in one direction, fitting is carried out again using two peaks. If derivative search yields two minima of the derivative in multiple directions, it is checked if the peaks giving rise to the multiple

\(^{10}\)The criteria mentioned in this section were determined by fitting 208 random overlaps of peaks for which the centre-of-mass and the integrated intensity were known. Using the values described here, consistent results were obtained in all cases.
3.3. Characterization of peaks

Figure 3.3: Example of the ‘chopping’ effect in the case of a real experiment. A single diffraction peak is present in successive diffraction images during the rotation in $\omega$. The spot is absent in the first image, appears in the second image, has maximum intensity in the third image, decreases in intensity and size in the fourth image and is absent in the fifth image. Darker pixels are higher in intensity. Each successive image differs in $\omega$ from the previous one by 0.3°.

minima (except the minimum in the derivative corresponding to the peak with the maximum intensity) are connected or not. If the multiple minima are connected, fitting is carried out again using two peaks, else the peak in the direction with the second highest (possible) maximum intensity in the region is chosen for fitting along with the peak with the maximum intensity. In the present implementation, only two peaks are searched for. The results of fitting are screened again according to the criteria described above.

(ii) There is only one peak in the search region (or two indistinguishable overlapping peaks) and the fit was unsatisfactory. In this case, the results of fitting are discarded and results from peak searching are assigned to the peak.

3.3.3 Merging in $\omega$

In the experiments where the mosaicity of the grains is greater than a function of the rotation step for the acquisition of diffraction images, $\Delta \omega$,$^{11}$ the diffraction peaks are present in multiple images, the so-called ‘chopping’ effect (Figure 3.3). These ‘chopped’ peaks appear at (almost) the same position on the detector and are defined to be overlapping in $\omega$. In ‘fast-mode’ 3DXRD, the centre-of-mass of the diffraction peaks is used for the determination of grain characteristics. Thus, all the ‘chopped’ peaks observed in multiple diffraction images originating from the same diffraction peak have to be merged into one to calculate the characteristics of the diffraction peak.

$^{11}$Mosaicity $> \arcsin \left( \sin \theta \cos \Delta \omega + \cos \theta \sin \eta \sin \Delta \omega \right) - \theta$

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3. Pre-processing of 3DXRD diffraction data

Once the results of fitting for all peaks have been screened, the second part of the algorithm merges the peaks overlapping in \( \omega \). Each diffraction image is assigned a corresponding \( \omega \) value, which is equal to the central orientation of the specimen during the acquisition of the diffraction image. In order to determine the peaks which are to be merged in \( \omega \), the algorithm checks for the peaks in successive images, the centre-of-mass of which lie within a distance of 1.7 pixels from each other.\(^{12}\) Ideally, this distance should be a function of \( \eta \). It has been found, however, that the chosen value of 1.7 pixels results in negligible error even for experiments using large numbers of grains. The position of the centre-of-mass of the peaks in terms of detector position \((y, z)\), or \((2\theta, \eta)\) for deformed grains and \(\omega\) is calculated by weighting according to the integrated intensity per diffraction image. The merged peaks are then corrected for the spatial distortion of the detector. Even though this step should ideally be carried out on individual pixels constituting the peaks before peak searching and not on the centre-of-mass of the peaks, this results in negligible error in the present case due to the small size of the peaks as compared to the length scale of the spatial distortions on the detector. The merged diffraction peaks characterized by the centre-of-mass position on the detector \((y, z)\) and in \(\omega\) are then called diffraction spots.

3.3.4 Limitations

Even though the current procedure has proven to be very effective and robust in resolving and characterizing overlapping peaks, a number of limitations remain.

(i) Maxima. Evidently, the ability of peak searching to successfully resolve overlapping peaks depends on the presence of multiple maxima. Peak fitting can, to some extent, detect overlapping peaks that do not consist of multiple maxima. However, in the present implementation, ‘hidden’ peak detection is successful only for relatively strong peaks when the centre-of-mass of the peaks are separated by a few pixels. Also, the present implementation tries to find ‘hidden’ peaks buried in shoulders of other peaks only if there is a single maximum in the region and only two peaks are fit, even if more than two peaks are found.

(ii) Too much overlap. In case the number of overlapping peaks is greater than six, it has been observed that the results of fitting become unsatisfactory. Using a

\(^{12}\)This is calculated, for typical 3DXRD setups such as the one described in §3.5.1.2, by taking the uncertainty in the position of the peaks, the maximum change in the orientation of the diffracting plane normal due to the change in \( \omega \) and the instrumental error for a detector with pixel size of 50 \( \mu \text{m} \).
different minimization routine can partially solve this problem. However, empirical and experimental studies have shown that this becomes a significant issue only for specimens consisting of more than 5000 undeformed grains.

(iii) Peak resolution. Due to the use of ‘far-field’ detectors with a limited spatial resolution, only a small number of pixels (~20 pixels) define a peak. For weak peaks, the number of pixels is often too low (below 10) to accurately define the shape of the peaks. In such cases, the shape of a peak cannot be defined with high accuracy and thus the results of fitting might be unsatisfactory. Furthermore, in the case of peaks present in the shoulder of other peaks, it becomes increasingly difficult to separate the two if the number of pixels is limited.

(iv) Deformed grains. On one hand, the shape of the peaks arising from deformed grains is well defined because of broadening due to increased grain mosaicity as compared to undeformed grains. On the other hand, the presence of broader peaks means that significant overlap is observed for lesser number of grains. Thus, depending on the mosaicity of the grains, there exists a limit to the maximum number of grains in the illuminated volume, which can be successfully characterized.

(v) Detector overflow. In case the maximum intensity of a peak exceeds the maximum intensity that the detector can handle, the pixels of the detector start to overflow. This results in, not only incorrect integrated intensity of the peak, but also asymmetric shape of the peaks.

(vi) Peak shape. The strength of the procedure lies in the possibility of fitting the shape of diffraction peaks with a symmetric shape function. However, in the case of ‘near-field’ detectors, the position of the detector close to the specimen means that the shape of the grains and their mosaicity dictates the shape of the peaks. Similarly, in the case of microstructures with inhomogeneous intra-grain deformations, the shape of the peaks is no longer regular. Thus, the present approach cannot be used. Although the irregular shape of the diffraction peaks arising from deformed grains can successfully be used to study the intra-grain dislocation structure by tweaking the experimental conditions, as shown by Jakobsen et al. [6], the present approach cannot be used.

(vii) Execution time. As compared to conventional peak search using a single threshold, watershed and fitting combined consume around 20 times more CPU time.\footnote{This time scales with the number of peaks per diffraction image.} However, the benefits of the technique far outweigh its computation speed since much larger number of grains can be successfully characterized with an im-
proved time resolution during the experiments as compared to scanning multiple layers. Furthermore, the choice of a 2D fitting function over a 3D fitting function leads to substantial improvement in the processing time without compromising the accuracy of the fitting.

3.4 Fitting global parameters of the experimental setup

For any mapping experiment, the accurate determination of the global (grain independent) parameters of the experiment is just as important as the accurate processing of the diffraction images. For single crystal diffraction, a number of techniques have been developed for accurate determination of the global parameters of the experiment [18 [19, 20, 21, 22]. In the literature, at least two independent techniques have been developed in order to determine the global parameters for ‘fast-mode’ 3DXRD: the method of Bernier et al. [12] and the method of Oddershede et al. [11]. The method of Bernier et al. [12] requires a calibration measurement using a standard powder specimen and a single crystal. In addition to the beam time required for such calibration measurements, for long experiments where beam and/or mechanical instabilities affect global parameters during the experiment [23], calibration measurements present obvious problems. On the other hand, the method of Oddershede et al. [11], which uses ImageD1114 for initial global parameter refinement, can, if the diffraction spots belonging to individual grains are successfully indexed15 by using approximate parameters, determine global parameters from the diffraction spots themselves. However, in the case of specimens consisting of a large number of grains, reliable indexing without accurate knowledge of the global parameters is impossible. Here a methodology is presented where all the global parameters can be determined from the experiment itself for large numbers of grains. The methodology has the added benefit during experiments because rough alignment of the specimen in the beam is enough to determine the global parameters accurately. Rough alignment means that aligning the specimen in the X−ray beam, in such a way that the specimen is in the beam during all rotations to be used in the experiment, is enough for accurate data analysis later. Exact alignment of the specimen in the centre of the beam and in the centre of the rotation axis is not required. The methodology has been developed for specimens with little to no deformation and in the case of significant deformations, the un−deformed parameters are used during indexing. The global parameters

14http://sourceforge.net/apps/trac/fable/wiki/imaged11
15Indexing is the procedure of assigning diffraction spots to individual grains.
3.4. Fitting global parameters of the experimental setup

for the deformed grains are refined later by using the diffraction spots indexed per grain using the undeformed parameters.

The global parameters can be subdivided into the parameters that affect the position of the diffraction spots on the detector and the parameters that affect the position of the diffraction spots in $\omega$ and will be dealt with in the same order.

3.4.1 Parameters affecting the position of the diffraction spots on the detector

The parameters that affect the position of the diffraction spots on the detector are specimen-to-detector distance ($L_{sd}$),\(^{16}\) lattice parameter ($a_0$), tilts of detector ($t_x$, $\beta$, $\gamma$) and the centre of the beam on the detector ($y_{cen}$, $z_{cen}$). Wedge also has an effect on the position of the diffraction spots on the detector, but it can be neglected during the determination of the aforementioned parameters. Although wavelength ($\lambda$) of the X-ray beam is also a parameter, it can be characterized very accurately during the experiment.

In the experiments involving high energy X-rays, it is not possible to fit both $L_{sd}$ and $a_0$ due to limitations posed by small Bragg angles. For example, for cubic structures, the relationship between $L_{sd}$ and $a_0$ is given as:

$$ R = L_{sd} \tan \left( 2 \arcsin \left( \frac{\lambda \cdot HKL_2}{2a_0} \right) \right) \quad (3.5) $$

where $R$ is the radius of the diffraction ring on the detector and $HKL_2 = \sqrt{h^2 + k^2 + l^2}$. For small Bragg angles, $\theta = \arcsin((\lambda \cdot HKL_2)/(2a_0))$, in high energy X-ray experiments, the relationship between $R$ and $HKL_2$ is approximately linear and thus, it is possible to choose multiple combinations of $L_{sd}$ and $a_0$ without affecting the result of Equation\(^3.5\). Therefore, as explained in §3.4.2, $a_0$ is determined by fitting the position of spots in $\omega$ in the present approach. For deformed grains, a single (mean) $a_0$ for all the grains is determined, which is refined later (per grain) using the diffraction spots assigned to individual grains during indexing.

Detector tilts are defined as three angles: $t_x$ is the rotation of the detector counter-clockwise around the direct beam axis ($x$-axis); $\gamma$ is the in-plane angle between the $z$-axis (as seen on the tilted detector) and the direction around which

\(^{16}\)Specimen-to-detector distance is actually a misnomer since it is, in reality, the distance between the axis of rotation and the detector.
the detector is tilted counter-clockwise by an angle $\beta$. Any point along this direction is common to both the tilted and the ideal detector. The definitions of $\beta$ and $\gamma$ are shown schematically in Figure 3.1 (b). The corrected azimuthal angle, $\eta$, is calculated as $\eta = \eta' + t_x + \eta_{\text{offset}} - \eta_{\text{diff}}$, where $\eta'$ is the azimuthal angle as seen on the tilted detector, $t_x$ is the tilt around the X-ray beam. The angles $\eta_{\text{offset}}$ and $\eta_{\text{diff}}$ are given as:

$$\eta_{\text{offset}} = -\gamma - \arctan (\tan (-\gamma) \cos \beta)$$

and

$$\eta_{\text{diff}} = \arctan \left( \frac{\tan (\eta' - \gamma)}{\cos \beta} \right) - \eta' + \gamma$$

The angle $\delta$ in Figure 3.1 (c) is given by

$$\delta = \frac{\sin (\eta - \gamma)}{\sin (\eta - \gamma)} \arccos \left( 1 - \sin^2 (\eta - \gamma) (1 - \cos \beta) \right)$$

The corrected radius, $R$, for the calculation of $2\theta$ is calculated as

$$R = \frac{L_s d R' \cos \delta}{L_s d + R' \sin \delta}$$

For fitting $\beta$, $\gamma$, $y_{\text{cen}}$ and $z_{\text{cen}}$, the sum of the squared difference between the observed diffraction angle ($2\theta_{\text{obs}}$) in the experiment and the calculated diffraction angle ($2\theta_{\text{calc}}$) according to an estimated value of $a_0$ is minimized. For undeformed grains, all the spots are first converted from detector coordinates ($y_{\text{det}}, z_{\text{det}}$) to lab coordinates ($x_{\text{lab}}, y_{\text{lab}}, z_{\text{lab}}$) and then to ($2\theta$, $\eta$).

The determination of $t_x$ is a bit more complex since $t_x$ affects the $\eta$ position of the diffraction spots and not the $2\theta$ position. Friedel pairs of reflections (reflections from $(hkl)$ and $(\bar{h}\bar{k}\bar{l})$ planes) are used in this case. In the 3DXRD setup, each $(hkl)$ plane comes in diffraction a maximum of two times during rotation around

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17The origin of the lab coordinate system is located at the intersection of the beam centre and the rotation axis. The coordinate system uses right hand notation with $x$-axis in the direction of the X-ray beam.

18Depending on the orientation of the plane, the number of times it comes under diffraction can be 0, 1 or 2.
3.4. Fitting global parameters of the experimental setup

ω over a full rotation of 360°. Once the effect of the position of the diffracting grain has been corrected, the symmetric properties of the Friedel pairs dictate that the η values of the two Friedel pairs are \( \eta_{FP}, (−180 + \eta_{FP}) \) and \( −\eta_{FP}, (180° − \eta_{FP}) \). However, for \( t_x \neq 0 \), these η values deviate from the ideal values due to the imperfect coordinate system. This is shown schematically in Figure 3.4, where spot 1 and spot 2 form a Friedel pair, separated in ω by 180°. In the tilted coordinate system shown in Figure 3.4, the spot 2 has \( \eta_2 = 180 − \eta_1 − 2t_x \), where \( \eta_1 \) is the η position of the spot 1. For a single Friedel pair, this equation can be used to solve for \( t_x \).

After detecting multiple Friedel pairs (using the approach described in Chapter 4), usually with \( |\eta| \approx 90° \), the imperfect η positions of the detected Friedel pairs are used to refine the value of \( t_x \). \( |\eta| \approx 90° \) is chosen in order to eliminate the effect of the \((x, y)\)–position of the diffracting grain, which is more difficult to correct for in the tilted coordinate system, on the observed values of η of the Friedel pair. Furthermore, as described in the next section, the effect of the wedge on the difference in ω for the Friedel pairs is negligible for \( |\eta| \approx 90° \). Detection of the Friedel pairs is simplified by their symmetric properties: the difference in ω is close to 180°, the difference in η is close to 180° and the integrated intensities of the diffraction spots are similar.

3.4.2 Parameters affecting the position of the diffraction spots in ω

In order to determine the parameters that affect the position of the diffraction spots in ω, consider the 3DXRD setup. According to the diffraction theory, a set of planes in a grain gives rise to a diffraction spot only when the Bragg diffraction criterion is met, that is, the angle between the normal to the planes and the incoming diffraction beam is \((\pi/2)−\theta\), where \( \theta \) is the Bragg angle. In 3DXRD, this condition is fulfilled multiple times at different ω intervals for all the grains in the illuminated volume during rotation of the specimen around the ω–axis. Thus, in case the setup is aligned perfectly, that is, the axis of rotation is orthogonal to the X–ray beam, the only parameters that determine ω for a diffraction spot are the parameters, which determine when the Bragg diffraction criterion is met, that is, the Bragg angle, \( \theta \), and the orientation of the diffracting plane normal. \( \theta \) itself is a function of the wavelength of the X–ray beam \( (\lambda) \) and \( a_0 \) of the specimen.

In addition to the parameters mentioned above, the only other parameter, which affects the position of the diffraction spots in ω is the wedge, defined as the deviation of the axis of rotation of the specimen from the ideal axis of rotation (orthogonal to the X–ray beam). The value of the wedge is determined by using Friedel
3. Pre—processing of 3DXRD diffraction data

Figure 3.4: Schematic of the effect of $t_x$ on the $\eta$ positions of the Friedel pairs. The spot positions are assumed to be already corrected for the position of the grain in the specimen. $(y, z)$ and $(y', z')$ are the ideal and tilted coordinate systems. The $\eta$ positions of spots 1 and 2 in the ideal and the tilted coordinate systems are $\eta_{FP}$, $(180 - \eta_{FP})$ and $\eta_1, \eta_2$, respectively.

Pairs. For a single diffraction spot from a $(hkl)$ plane, two types of Friedel pairs exist corresponding to the two times the $(\bar{h} \bar{k} \bar{l})$ plane is in diffraction. Out of the four diffraction spots belonging to the Friedel pairs, two Friedel pairs are separated by $180^\circ$ in $\omega$, but the $\omega$—difference ($\omega_{\text{diff}}$) for the other two Friedel pairs is a function
of \( (\eta, \theta) \). If wedge is absent, \( \omega_{\text{diff}} \) for the ‘symmetric’ Friedel pairs is 180°. For non-zero values of the wedge and depending on the orientation of the diffracting plane normal (defined by \( \eta \)), \( \omega_{\text{diff}} \) for ‘symmetric’ Friedel pairs deviates from the ideal value of 180°. The deviation from the ideal value of \( \omega_{\text{diff}} = 180^\circ \) between the Friedel pairs for two values of the wedge is shown in Figure 3.5 (a) as a function of \( \eta \). For example, for spots present at \( \eta = 90^\circ \), the effect of small values of the wedge is negligible whereas for spots present at \( \eta = 0^\circ \), the corresponding spot for the Friedel pair can be totally absent \( (|\sin \eta| \to 0) \). It can be seen from Figure 3.5 (a) that the Friedel pairs with low values of \( |\sin \eta| \) are more sensitive to different values of wedge than the Friedel pairs with high values of \( |\sin \eta| \) and thus Friedel pairs of the former quality are used. Alternatively, Wright et al. have proposed a methodology for ultra-precise determination of \( \omega \) values of the diffraction spots \[24\]. The wedge is fit by identifying a number of Friedel pairs for multiple grains and multiple \( \eta \) values and calculating the corresponding \( \omega_{\text{diff}} \) for each pair.

In the experiments where \( a_0 \) of the specimen is not known accurately, the unique symmetric properties of Friedel pairs can again be used. \( \omega_{\text{diff}} \) for ‘asymmetric’ Friedel pairs \( (\omega_{\text{diff}} \neq 180^\circ \) after correction for wedge) as a function of \( \eta \) for multiple values of \( 2\theta \) is shown in Figure 3.5 (b). For \( |\sin \eta| = 1 \), \( \omega_{\text{diff}} \) is exactly equal to \( 2\theta \). From Figure 3.5 (b) it can be seen that for a certain combination of \( \omega_{\text{diff}} \) and \( \eta \), only a single value of \( 2\theta \) is possible. Thus, in case \( \omega_{\text{diff}} \) and \( \eta \) for a Friedel pair are known, \( 2\theta \) and correspondingly the \( a_0 \) can be determined. Similar to the case of fitting of the wedge, Friedel pairs with low values of \( |\sin \eta| \) are used due to higher sensitivity as compared to Friedel pairs with high \( |\sin \eta| \). By using an initial guess for \( a_0 \), all the ‘asymmetric’ Friedel pairs are identified. Later, \( a_0 \), which defines \( \theta \), is fit by using \( \eta \) and \( \omega_{\text{diff}} \) for the ‘asymmetric’ Friedel pairs.

During the determination of both wedge and \( a_0 \), the \( \eta \) position of the Friedel pairs is corrected for the position of the diffracting grain with respect to the centre of rotation of the specimen when the grain was in diffraction. This is important because both the procedures are sensitive to the \( \eta \) position of the diffraction spots. Furthermore, \( t_x \) is determined before fitting wedge and \( a_0 \) for the same reason.

### 3.4.3 Implementation

The routines for fitting global parameters have been implemented in MATLAB\textsuperscript{R}. Minimization of the differences is carried out using the \texttt{fmincon}\textsuperscript{19} function in

\[\text{http://www.mathworks.com/help/toolbox/optim/ug/fmincon.html}\]
3. Pre-processing of 3DXRD diffraction data

Figure 3.5: Effect of η on the difference in ω (ω_{diff}) for Friedel pairs for different values of (a) wedge and; (b) 2θ. (a) Deviation from the ideal value of ω_{diff} = 180° for the 'symmetric' Friedel pairs as a function of η is shown for two values of the wedge. (b) ω_{diff} for the 'asymmetric' Friedel pairs as a function of η is shown for four values of 2θ. For |sin η| = 1, ω_{diff} for the asymmetric Friedel pairs is exactly equal to 2θ. For |sin η| = 0, the asymmetric and the symmetric Friedel pairs overlap.
MATLAB®. In order to find the global minimum of the function, MultiStart function in MATLAB® is used to call \texttt{fmincon}. MultiStart uses multiple initial guesses within the search range in order to find a number of local minima. Thus, if enough initial guesses are used, global minimum can be successfully found. The final outputs are two ASCII format files, one with the refined parameters and the other with location of the diffraction spots corrected for all parameters.

### 3.5 Test cases

The programs have been tested thoroughly using simulated and real datasets in order to identify the strengths and the limitations of each program.

#### 3.5.1 Peak searching and peak fitting

Diffraction peaks are characterized by the position on the detector, the position in $\omega$ and the integrated intensity. In order to test the results of peak searching and peak fitting, the accuracy in the knowledge of these parameters is evaluated, first by using simulated peaks and then by using a real dataset.

##### 3.5.1.1 Simulated data

Two representative examples to validate the algorithms will be shown here. The first example consists of a diffraction image containing a region with two overlapping peaks with one distinct maximum, with the second peak buried in the shoulder of the first one. Peak searching was carried out on the image with a threshold of 150 counts (the maximum intensity was 1500 counts and background around 100 counts). As expected, peak searching detected one peak instead of the two present. However, fitting was able to correctly identify the missing peak. The results are summarized in Table \ref{table:peak_results}. This highlights the fact that not only is a peak missing if a single thresholding operation, or no fitting, is carried out, but also centre—of—mass of the peak that is found is incorrect. Furthermore, it can be seen that after fitting, the error in position on the detector is much smaller than one pixel, even though the error in integrated intensity is not negligible. This is because the integrated intensity during fitting is calculated by summing up the intensity from all the pixels with intensity higher than the minimum threshold, whereas the input integrated intensity includes the pixels below the minimum threshold as well.

\begin{table}[ht]
\centering
\begin{tabular}{ |c|c|c| }
\hline
Peak & Found Position & Real Position \\
\hline
Peak 1 & 150 & 100 \\
Peak 2 & 120 & 80 \\
\hline
\end{tabular}
\caption{Peak results comparison}
\end{table}

\footnote{Peak 1 and Peak 2 were identified as one during peak searching. The error in position is calculated between the peak found from peak searching and the real Peak 1 and Peak 2.}
3. Pre—processing of 3DXRD diffraction data

Table 3.1: Overview of the results from peak searching and peak fitting for the simulated dataset with one region with two overlapping peaks and one maximum.

<table>
<thead>
<tr>
<th>% Error in integrated intensity</th>
<th>Error in position on detector (pixels)</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak searching</td>
<td>Fitting</td>
<td>Peak searching</td>
<td>Fitting</td>
</tr>
<tr>
<td>Peak1</td>
<td>N.A.</td>
<td>1.095</td>
<td>7.4731</td>
</tr>
<tr>
<td>Peak2</td>
<td>N.A.</td>
<td>1.158</td>
<td>-10.3135</td>
</tr>
</tbody>
</table>

Table 3.2: Overview of the results from peak searching and peak fitting for the simulated dataset with six overlapping peaks.

<table>
<thead>
<tr>
<th>% Error in integrated intensity</th>
<th>Error in position on detector (pixels)</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak searching</td>
<td>Fitting</td>
<td>Peak searching</td>
<td>Fitting</td>
</tr>
<tr>
<td>Peak1</td>
<td>9.694</td>
<td>1.227</td>
<td>-1.2085</td>
</tr>
<tr>
<td>Peak2</td>
<td>-5.492</td>
<td>1.207</td>
<td>0.9923</td>
</tr>
<tr>
<td>Peak3</td>
<td>-6.200</td>
<td>1.239</td>
<td>-0.9959</td>
</tr>
<tr>
<td>Peak4</td>
<td>15.641</td>
<td>1.150</td>
<td>0.9713</td>
</tr>
<tr>
<td>Peak5</td>
<td>1.982</td>
<td>1.198</td>
<td>-0.7570</td>
</tr>
<tr>
<td>Peak6</td>
<td>-3.493</td>
<td>1.191</td>
<td>0.6935</td>
</tr>
</tbody>
</table>

The second example consists of a diffraction image containing a region with six overlapping peaks, each with a distinct maximum. The different steps of peak searching are shown in Figure 3.6. Again peak searching was run with the same settings as in the previous case. All the 6 peaks were identified successfully. The results of peak searching and peak fitting are shown in Table 3.2. It can be seen that the error in position after fitting is very small. The error in integrated intensity can again be attributed to the intensity from the pixels below the minimum threshold.

3.5.1.2 3DXRD experiment

The 3DXRD experiment was carried out at beamline ID11 of European Synchrotron Radiation Facility (ESRF), Grenoble, France. A spark cut steel specimen (composition: 0.011 wt% C, 0.87 wt% Mn, balance Fe, diameter 1 mm) was placed in a specially designed furnace and heated to a temperature of 900 °C. The specimen was held at the annealing temperature for 3 h in order to get large austenite...
Figure 3.6: Schematic description of the results of the different processing steps during peak searching. The background is white in each image. (a) The initial region containing six peaks. Darker pixels have positive intensity. (b) Result of the seeded watershed operation. Different colours show pixels belonging to different grains. Black pixels are the watershed (or border) pixels whereas white is the background. (c) Result of thresholding operation using the threshold calculated from the maximum intensity of the border pixels belonging to each peak. Black pixels have non-zero intensity.
grains. The X-ray beam, 300 µm high and 1200 µm wide, was calibrated to the energy of 88.005 keV (Pt edge) using a Laue-Laue setup. Around 1600+ grains in the specimen were illuminated in this way. A FReLoN—4M detector [26] with 2048 x 2048 pixels of 50 x 50 µm size was placed at a distance of ∼325 mm from the specimen. At the end of isothermal annealing, diffraction images were acquired for $\omega \in \left[ \!\left[ -130.05^\circ; -46.95^\circ \right] \cup \left[ 49.95^\circ; 133.35^\circ \right] \!\right]$ in 0.3° steps. With this setup, the first four Debye—Scherrer rings for the austenite phase (F.C.C.) are completely visible on the detector. A total of 560 diffraction images were thus recorded.

The corrected diffraction images were processed with peak searching using 150 counts as the threshold (the background is around 100 counts). The peaks with maximum intensity above 58000 counts were separated as saturated peaks due to detector overflow. The connectivity used was 8—connected neighbourhood. An intensity one count higher than the highest intensity in the border pixels was used for thresholding after watershed. Afterwards, using the aforementioned parameters, all the peaks found with peak searching were fit. The maximum number of times the algorithm is allowed to update the values of the parameters (or the fit function) was set to $10^6$. On a computer equipped with a 3.0 GHz Dual—Core Intel® processor, the processing time was 2 s per image for peak searching and 12 s per image for fitting for an average of 212 peaks per image.

Comparison of the results from peak searching and fitting is shown in Figure 3.7. Figure 3.7 (a) shows that the integrated intensity from fitting is slightly underestimated. In part, this is due to the relatively large amount of intensity that falls below the threshold for the small diffraction peaks. From 3.7 (b), it can be seen that for most of the peaks, the difference in the position on the detector between the results of peak searching and peak fitting is very small. The average difference in position (absolute value) was found to be 0.0829 pixels. This translates into an error in position of the diffraction spots equal to ∼4 µm. The final results are summarized in Table B.3. Out of the 119104 peaks found, 115810 peaks could be successfully fit using the criteria described before, a success rate of 97.23%. In case only a threshold of 150 counts had been used without watershed or fitting, only 109660 peaks would have been found, with 9444 peaks (or 17012 overlapping peaks) being incorrect. In the dataset, 102092 peaks (85.71%) were detected as non—overlapping. Out of the 3294 peaks that could not be successfully fit, 1319 were smaller than 10 pixels, which indicates that the peaks were not big enough to define a good shape. 309 peaks failed the maximum intensity criterion and 51 peaks were part of regions consisting of more than 6 peaks, the maximum number which is fit (the rest were still fit satisfactorily).
3.5. Test cases

Figure 3.7: Results of peak searching and peak fitting on the experimental dataset. (a) Histogram of the error in the integrated intensity calculated as the difference in the intensity calculated according to fitting result and the intensity present in the fitting regions. (b) Histogram of the difference in the position on the detector between the results of peak fitting and peak searching for the peaks, which passed the criteria for determining a successful fit.
3. Pre-processing of 3DXRD diffraction data

Table 3.3: Overview of the results from peak searching and fitting on the experimental dataset.

<table>
<thead>
<tr>
<th>Number of peaks per region</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>&gt;6</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of regions</td>
<td>102092</td>
<td>6206</td>
<td>1006</td>
<td>245</td>
<td>79</td>
<td>21</td>
<td>11</td>
<td>109660</td>
</tr>
<tr>
<td>Number of peaks</td>
<td>102092</td>
<td>12412</td>
<td>3018</td>
<td>980</td>
<td>395</td>
<td>126</td>
<td>81</td>
<td>119104</td>
</tr>
<tr>
<td>Number of peaks successfully fit</td>
<td>100364</td>
<td>11477</td>
<td>2658</td>
<td>832</td>
<td>239</td>
<td>99</td>
<td>51</td>
<td>115810</td>
</tr>
</tbody>
</table>

3.5.2 Global parameters – simulated data

In order to test the accuracy of the fitting of the global parameters, simulation of a 3DXRD experiment was performed with PolyXSim, the FABLE polycrystal simulator. A specimen consisting of 1000 grains of austenite (F.C.C., $a_0 = 3.55$ Å) was chosen for the simulation. In Chapter 4, simulations of specimen consisting of 3000 grains are shown. The grains, with random crystallographic orientations and sizes, were positioned randomly in a cylindrical volume of 500 μm radius and 300 μm height. Strains, using a Gaussian distribution with mean $\mu = 0$ and width $\sigma = 10^{-5}$, were introduced in the grains. A virtual detector identical to the FReLoN−4M detector placed at a distance of 315696 μm from the specimen was used in the simulations, with the X−ray energy set to 88.005 keV (Pb−edge). Diffraction spots were simulated for $\omega \in [-180°; 180°]$.

To judge the quality of fit of the global parameters, a number of starting guesses of the different parameters were used. The procedure followed was: first $\beta$, $\gamma$, $L_{sd}$, $y_{cen}$ and $z_{cen}$ were fit by minimizing the difference in the observed and the expected $2\theta$ values. Since an initial guess of $a_0$ (3.54 Å instead of 3.55 Å) was used, the fit value of $L_{sd}$ was considerably different from the real value of $L_{sd}$. A total of 1300 Friedel pairs were then identified and used, in order, to determine $t_x$, wedge (both using ‘symmetric’ Friedel pairs with $\omega_{\text{diff}} = 180°$) and $a_0$ (using ‘asymmetric’ Friedel pairs with $\omega_{\text{diff}} \neq 180°$). The fit value of $a_0$ was then used to refine $\beta$, $\gamma$, $L_{sd}$, $y_{cen}$ and $z_{cen}$ again. The resulting position of the diffraction spots after corrections was compared to the ideal position of the diffraction spots. The errors calculated from the fit that gave the worst output are shown in Figure 3.8. The final global parameters were off by 0.5 μm in $L_{sd}$, 0.02 pixels (1 μm) in $y_{cen}$

\[^{21}\text{http://sourceforge.net/apps/trac/fable/wiki}\]
Figure 3.8: Error in the position of the diffraction spots calculated using the ideal global parameters and the fit global parameters. Histogram of the error in (a) the position in $y$ and $z$ and; (b) the position in $\omega$. 
and $z_{cen}$, 0.0008° in $\beta$, 0.002° in $\gamma$, 0.0005° in $t_x$, 0.0007° in wedge and 0.0003 Å in $a_0$. The position of the diffraction spots on the detector and in $\omega$ was, on average, 0.7 µm and 0.0002° off from the ideal position, respectively. For the best fit, the final global parameters were off by 0.2 µm in $L_{sd}$, 0.014 pixels (0.7 µm) in $y_{cen}$ and $z_{cen}$, 0.0003° in $\beta$, 0.0013° in $\gamma$, 0.0003° in $t_x$, 0.0004° in wedge and 0.00017 Å in $a_0$.

3.6 Summary

A set of algorithms for the pre-processing of 2D diffraction data acquired using thousands of grains are presented consisting of two steps, namely, characterization of diffraction peaks and determination of global parameters. The procedure for the characterization of peaks is designed to successfully solve the long-standing problem of 2D peak overlap in 3DXRD-type of experiments. The procedure consists of a watershed operation to detect the number of peaks present in the images and compute parameters for initialisation. The initialisation parameters obtained from watershed are used to fit the peaks to a 2D pseudo-Voigt function in order to refine the centre of mass of the peaks on the detector. After a merging step in $\omega$ the diffraction spots are characterized by the position of the centre-of-mass of the spots in terms of ($y$, $z$ and $\omega$) for undeformed grains and ($2\theta$, $\eta$ and $\omega$) for deformed grains. The technique presented is capable of handling data acquired from a large number of grains with considerable peak overlap. The algorithms are validated using both simulated and experimental data. Furthermore, a technique for accurate determination of global parameters of the experiments is developed. The technique eliminates the requirement of calibration measurements and has been verified using simulations. This helps in simplifying the experiments and the subsequent data analysis. The results of the operations described in the present chapter are fed into a novel indexing and fitting routine described in Chapter 4 to calculate the grain characteristics. The codes described in this Chapter may be obtained from [https://sourceforge.net/projects/short3dxrd](https://sourceforge.net/projects/short3dxrd).

3.7 Bibliography


3. Pre—processing of 3DXRD diffraction data


3.7. Bibliography


**Abstract**

A procedure for the determination of grain characteristics of thousands of grains from data acquired using 3-Dimensional X-Ray Diffraction (3DXRD) is presented. The developed approach is orders of magnitude faster than the presently available approaches for indexing of thousands of grains. Using the information obtained from the steps described in Chapter 3, volume, crystallographic orientation, centre—of—mass position and strain state of the grains in the volume illuminated by the X-ray beam can be determined. The algorithms dealing with the determination of orientation, centre—of—mass position and strain state of the grains are divided into two parts: first dealing with indexing, i.e., assigning the diffraction spots to individual grains assuming un—strained lattice and second dealing with refinement of the crystallographic orientation, centre—of—mass position and strain state.
Determining the state of the grains using the diffraction spots assigned during indexing. The different approaches to indexing that exist in literature are presented and compared with the novel approach developed here.

The indexing procedure described in §4.1 can be run in two modes depending on the number of grains. For large numbers of grains, the approach employs a novel specimen ‘surface’ scanning technique in combination with a reduced number of search orientations to achieve high robustness and computation efficiency. For unstrained specimens, both the modes of indexing and the subsequent process of refinement are validated using simulated data for 60 and 3000 grains. In both the cases, the centre-of-mass position of the grains was determined with a mean error of 0.7 µm and the orientation was determined with a mean error of 0.0003°. Furthermore, an experiment was ‘mimicked’ by introducing experimental errors in the simulation for 3000 grains. The resulting mean errors in centre-of-mass position (2.1 µm) and orientation (0.008°) of the grains are higher than those for the ideal simulations and the errors in an experiment will depend on the ‘true’ experimental errors. The algorithms dealing with strained specimens are validated using a simulation for 3000 grains with ‘mimicked’ experimental errors. The centre-of-mass position, the crystallographic orientation, the normal strain tensor components and the shear strain tensor components of the grains were determined with a mean error of 8 µm, 0.006°, 5.2 × 10⁻⁵ and 2.8 × 10⁻⁵, respectively.

Further building up on the indexing approach described in §4.1 §4.2 describes an advanced indexing approach using the symmetric properties of Friedel pairs. The approach uses both symmetric and asymmetric Friedel pairs to reduce the search surface in the specimen to a straight line for each possible Friedel pair. This allows for a speed up of around 40 times during computation. Indexing of the 3000 grains simulation shows that highly accurate results can be obtained in minutes. Furthermore, the first results of indexing of experimental data acquired from a specimen consisting of more than 2200 grains in the illuminated volume are shown.

The possibility of obtaining grain-level information for thousands of grains with high speed of acquisition makes the technique very attractive for in-situ studies of thermo-mechanical processes in polycrystalline materials.
4.1 Indexing using a surface scanning technique

4.1.1 Introduction

In the last decade, a number of techniques have been developed for non-destructive characterization of three-dimensional (3D) microstructures of polycrystalline materials using high energy X-ray diffraction available at 3rd generation synchrotron sources. A few examples include Differential Aperture X-Ray Microscopy, DAXM [1], 3D X-Ray Diffraction microscopy, 3DXRD [2,3], and Diffraction Contrast Tomography, DCT [4]. DAXM has nanometre resolution, but requires time-consuming acquisition strategies and is limited to relatively small volumes. 3DXRD and DCT, which can be considered a variant of 3DXRD, allow for simultaneous characterization of volume, crystallographic orientation and stresses in bulk microstructures with micrometre resolution. These two techniques have been used to investigate changes in polycrystalline materials at the microstructural level and have led to better understanding of the complex processes involved during heat treatments and deformation of materials [2,5,6,7,8]. In general, 3DXRD can be used in three modes. In the ‘fast mode’, the average characteristics of each grain (that is, volume, position of centre-of-mass, crystallographic orientation and average strain state) can be obtained with a time resolution of the order of a few minutes. In the ‘slow mode’, grain shape, location and crystallographic orientation can be mapped with a time resolution of the order of a few hours. In the ‘high-resolution mode’, crystallographic orientation and strain of individual crystals can be mapped in the reciprocal space again with a time resolution of the order of a few hours. A full overview of the technique can be found elsewhere [9].

In Chapter 3 a data analysis strategy for the characterization of overlapping diffraction peaks and the determination of global (grain-independent) parameters for experiments carried out using ‘fast-mode’ 3DXRD and with specimens containing a large number of grains was described. This chapter continues with the data analysis to present a procedure for the characterization of four properties of grains, namely, grain volume, crystallographic orientation, centre-of-mass position and strain state. The aim of this section is to validate the algorithms with simulated data and the results of analysis of experimental data will be shown in §4.2.

Currently there exist four different methods for indexing polycrystal diffraction data acquired using ‘fast-mode’ 3DXRD: Bernier et al. [10]; Moscicki et al. [11];
4. Determination of volume, centre of mass, crystallographic orientation and strain state of grains

ImageD11\textsuperscript{1} [12] and GrainSpotter\textsuperscript{2} [12, 13]. Out of the four, the program from Bernier \textit{et al.} [10] and GrainSpotter [12] can handle the maximum number of grains simultaneously (up to a thousand). It must be noted here that although the DCT technique [4] is capable of processing up to 2500 grains, it suffers from three limitations: (i) the use of high resolution detectors limits the time resolution; (ii) rotation of the sample over 360° is required and; (iii) deformed grains cannot be handled presently. The new approach laid out in the present chapter uses a novel combination of a reduced number of possible grain centre−of−mass positions and orientations, allowing for the characterization of more than 3000 grains in a robust and time efficient manner. This opens new possibilities for \textit{in−situ} studies involving close−to statistically representable number of grains with high time resolution.

4.1.2 3DXRD technique: setup and principles

Details of the setup of ‘fast−mode’ 3DXRD were given in Chapter 3 and will be described briefly here (Figure 4.1). The specimen, placed on top of an $\omega$ rotation setup, is illuminated by a collimated monochromatic X−ray beam. All regions in the specimen volume illuminated by the X−ray beam that satisfy the Bragg diffraction condition for a particular orientation of the specimen generate a diffracted beam giving rise to a signal on a 2D detector placed relatively far from the specimen (≈20−50 cm). In order to get all grains in the illuminated volume under diffraction a number of times, the specimen is rotated around the $\omega$−axis perpendicular to the X−ray beam. This setup means that diffraction spots appear at the intersection of the Debye−Scherrer cones (of vertical angle $4\theta$) and the detector plane, so−called diffraction rings. The integrated intensity of a diffraction spot is directly proportional to the volume of the corresponding grain and the position of the diffraction spot on the diffraction ring arising from a diffracting plane is governed by the orientation of the plane. Furthermore, depending on position of the grain with respect to the beam centre (intersection of vertical centre of the X−ray beam and rotation axis) when it is under diffraction, the diffraction spot may be displaced from idealized position on the diffraction ring. An example of a diffraction image in this geometry shown in Figure 4.2 highlights this displacement.
4.1. Indexing using a surface scanning technique

Figure 4.1: Schematic of the fast-mode 3DXRD setup with the far-field detector. The dimensions are not to scale. The angles $2\theta$, $\omega$, and $\eta$ are defined.
4. Determination of volume, centre of mass, crystallographic orientation and strain state of grains

4.1.2.1 Grain volume

The volume of a grain, \( V_g \), is related to the integrated intensity of the corresponding diffraction spot, \( I_g \), as \([8, 14]\):

\[
V_g = \frac{1}{2} m_{hkl} \cos \theta \cdot V_{gauge} \frac{I_g}{k I_p} \Delta \theta
\]  

(4.1)

where \( m_{hkl} \) is the multiplicity of the \((hkl)\) plane, \( \theta \) is the Bragg diffraction angle, \( V_{gauge} \) is the illuminated volume defined by intersection of the X-ray beam and the specimen, \( k \) is the number of diffraction images in which the diffraction spot is present, \( I_p \) is the powder intensity (intensity per diffraction ring on the image if the specimen were a powder) and \( \Delta \theta \) is the angle over which the diffracting plane normal is rotated while the grain is in diffraction, given by

\[
\Delta \theta = \arcsin \left( \sin \theta \cos \Delta \omega + \cos \theta |\sin \eta| \sin \Delta \omega \right) - \theta
\]  

(4.2)

where \( \Delta \omega \) is the total rotation of the specimen during which the grain was in diffraction and \( \eta \) is the azimuthal angle defined in Figure 4.1.

During the pre-processing of diffraction images, described in Chapter 3, a low threshold is chosen in order to define regions with intensity from grains in the specimen. Thus, this threshold defines the minimum intensity of diffraction spots that can be detected. For a fixed minimum \( I_g \), defined by the threshold, the minimum volume of grains that can be detected for a given experiment is a function only of \( \eta \) and \( \theta \). From Equations 4.1 and 4.2, it can be derived that \( V_g \) increases with increasing \( \theta \) and increasing \( |\sin \eta| \). Thus, the technique has highest detection sensitivity for grains that diffract in innermost ring (ring with minimum \( \theta \)) close to poles of the diffraction ring (\(|\sin \eta| \rightarrow 0\)). For instance, the minimum volume of grains that are observed at \( \theta = 4.88^\circ \) and \( \eta = 90^\circ \) is roughly 50 times larger than at \( \theta = 1.99^\circ \) and \( \eta = 9^\circ \).

4.1.2.1.1 Limitations

The availability of high-intensity, high-energy X-rays at 3rd generation synchrotron sources allows for the possibility of capturing signals from a very wide range of grain sizes in a short period of time. This is especially useful during in-situ treatments where time resolution is important. A number of examples will be shown in Chapters 5, 6 and 7. However, the technique has a number of limitations:
4.1. Indexing using a surface scanning technique

Figure 4.2: Example of a diffraction image recorded using the ‘fast-mode’ 3DXRD setup. The specimen used was Fe–2wt%Mn, heated to a temperature of 1000°C in order to have 100% austenite (F.C.C.) phase. Dark regions show pixels with positive intensity. The solid rings indicate the expected location of Debye–Scherrer rings for the austenite phase at 1000°C for the following \(\{hkl\}\) planes (radially outwards): \{111\}, \{200\}, \{220\} and \{311\} for grains positioned at \((0,0,0)_{lab}\) in the specimen. Inset: The deviation of diffraction peaks from the ideal location at the diffraction rings due to the effect of positioning of the diffracting grain inside the specimen.
4. Determination of volume, centre of mass, crystallographic orientation and strain state of grains

(i) The dynamic range of the detectors available limits the maximum width of grain size distributions that can be studied. For example, if the signal from both very small and very large grains is acquired, only one of the two sizes ranges can successfully be characterized. If the acquisition time is increased in order to study small grains, the signal from large grains will be very high, resulting in detector overflow. On the other hand, reducing the acquisition time to study large grains would result in lower signal from small grains, which would fall below the threshold.

(ii) The inaccuracy in the grain volume depends on the grain size because the application of a single, uniform threshold means that any signal below the threshold is lost. In the case of undeformed grains, the diffraction peaks have a sharp profile, meaning that for large grains, the intensity lost below the threshold is negligible. However, for small grains, the intensity that is lost below the threshold can be a significant fraction of the total intensity from the grains.

(iii) As explained in above, the smallest grains that can be observed depend strongly on the location of the diffraction spot in $\eta$ and the diffraction angle, $\theta$. Thus, not all diffraction spots from small grains are characterized during the data analysis.

(iv) The choice of the rotation step, $\Delta \omega$, is crucial for the calculation of grain volumes. If the mosaicity of the grains is significantly smaller than $\Delta \theta$ (which depends on $\Delta \omega$), the volume of the grains is overestimated. This is because the derivation of Equation 4.1 assumes that each grain is in diffraction at all times during acquisition of the diffraction image in which the diffraction spot is observed.

4.1.2.2 Grain orientation and position

In order to define the grain orientation and position and their effect on the position of the diffraction spots on the detector, four Cartesian coordinate systems are introduced: the specimen system, the grain system, the laboratory system and the detector system. These are denoted by the subscripts $s$, $g$, $lab$ and $det$, respectively. The detector coordinate system is the same as the laboratory coordinate system except that the origin is located at the detector instead of at the centre of rotation of the specimen. The orientation of a grain is given by the $3 \times 3$ orthogonal matrix, $U$, defined as follows [15]:

$$n_s = U \cdot n_g$$

(4.3)
where \( n \) is an arbitrary direction in the corresponding co–ordinate system.

In 3DXRD, the specimen is rotated about an axis perpendicular to the incident X–ray beam. A unit vector in the direction of the rotated normal to a plane is given as

\[
\begin{align*}
n_{\text{lab}} = \begin{pmatrix} x_{\text{lab}} \\
y_{\text{lab}} \\
z_{\text{lab}} \end{pmatrix} &= \Omega \cdot n_s = \begin{pmatrix} \cos \omega & -\sin \omega & 0 \\ 
\sin \omega & \cos \omega & 0 \\ 
0 & 0 & 1 \end{pmatrix} \cdot n_s \\
\end{align*}
\]

(4.4)

where \( \omega \) is the angle by which the specimen has been rotated. In transmission geometry, diffraction event from a plane takes place when the angle between the normal to the plane and the incoming X–ray beam is equal to \((90^\circ - \theta)\). This can be written as

\[
\cos(90^\circ - \theta) = n_{\text{lab}} \cdot n_{\text{beam}}
\]

(4.5)

where \( n_{\text{beam}} \) is a unit vector in the direction opposite to the direction of the incoming X–ray beam. Solution to Equation 4.5 yields the value of \( \omega \) when a diffraction event from the plane takes place. For all the allowed values of \( \omega \), Equation 4.5 can have 0, 1 or 2 solutions depending on \( \theta \) and \( n_s \).

Correspondingly, for a grain positioned at \((a, b, c)\) in the specimen co–ordinate system, the position of the grain after rotation in the laboratory coordinate system is

\[
\begin{pmatrix} a_{\text{lab}} \\
b_{\text{lab}} \\
c \end{pmatrix} = \Omega \cdot \begin{pmatrix} a \\ 
b \\ 
c \end{pmatrix}
\]

(4.6)

The position of the diffraction spot on the detector in the detector coordinate system is then given by

\[
\begin{align*}
(y_{\text{det}} = b_{\text{lab}} &- (L_{sd} - a_{\text{lab}}) \tan 2\theta \sin \eta) \\
(z_{\text{det}} = c + (L_{sd} - a_{\text{lab}}) \tan 2\theta \cos \eta)
\end{align*}
\]

(4.7)

where \( L_{sd} \) is the distance between the detector and the centre of rotation and \( \eta \) is given by
4. Determination of volume, centre of mass, crystallographic orientation and strain state of grains

\[ \eta = \arctan \left( -\frac{y_{lab}}{z_{lab}} \right) \]  \hspace{1cm} (4.8)

4.1.3 Indexing

The procedure of assigning diffraction spots to individual grains is commonly referred to as indexing. The classical approaches to indexing are introduced first and then the approach developed is explained.

4.1.3.1 Classical approaches

4.1.3.1.1 Forward projection

Forward projection encompasses scanning the full orientation space in small steps and simulating diffraction events at each step. The simulated position of the diffraction spots is compared with the observed position of the diffraction spots. All the grains in the illuminated volume are assumed to be present at \((0, 0, 0)_{lab}\). The orientations for which a minimum number of observed diffraction spots are found within a pre-defined margin from the simulated position are stored as belonging to individual grains \([13, 16]\). This technique works well for a small number of grains, but if the number of grains in the illuminated volume is large, the chance of false hits becomes high due to the large margins required since the position of the grains in the specimen is not taken into account. Therefore, for large numbers of grains, the effect of the position of the grains in the specimen can be taken into account by combining the orientation space scan with the mapping of a grid in the specimen volume. At each point on the grid, all orientations are simulated. This way, the margins used for matching the observed and the simulated diffraction spots can be kept low. However, depending on the step size of the grid, this can be a very computationally intensive operation, but, is independent of the number of grains in the specimen and can handle a very large number of grains.

A variation of this approach is used in GrainSpotter\(^3\) \([12, 13]\) where the scattering vectors for a number of random orientations (or discretised points in the full orientation space) are scanned and matched with the observed scattering vectors. However, since the position of the diffracting grains are not taken into account during indexing, large margins are required, which limit the applicability of the method for indexing large numbers of grains. For ‘slow-mode’ 3DXRD employing

\[ \text{http://sourceforge.net/apps/trac/fable/wiki/grainspotter} \]
4.1. Indexing using a surface scanning technique

high resolution detectors, a full orientation space and specimen scanning method has been implemented by Suter et al. [17].

4.1.3.1.2 Backward projection  This approach uses observed diffraction spots to group the diffraction spots together. In the 3DXRD diffraction geometry, if the diffracting grain is present at \((0, 0, 0)_{lab}\), every diffraction spot can be represented as a straight line in the Rodrigues–Frank (RF) orientation space [18]. The orientation of the grain lies on this line. In order to find the real orientation of the grain, lines from each observed diffraction spot are calculated in RF space and all the lines which intersect at a single point are stored as belonging to a grain. In the case that the grain is not present at \((0, 0, 0)_{lab}\) (and accounting for experimental errors), each of these lines becomes a volume in the orientation space. The intersection of these volumes is no longer a point, but a volume. For a small number of grains, this intersection volume can be identified successfully. However, if the number of grains is large, the probability of successful indexing lowers due to an increased chance of false hits. Computation time scales with the number of diffraction spots. There exist two methods from Moscicki et al. [11] and Bernier et al. [10] that follow a modification of this approach to (partly) mitigate the problems posed for moderately large numbers of grains. Moscicki et al. [11] employ the unique properties of Friedel pairs in order to group multiple diffraction spots belonging to the same grain. This technique works very well for a small ensemble of grains. The technique of Bernier et al. [10] uses the observed diffraction spots in order to define search fibres (straight lines in RF space) in the orientation space that are discretized and matched with the observed diffraction spots. Since the orientation space is only scanned along orientation fibres, the technique is computationally more efficient than the full forward projection techniques. However, similar to GrainSpotter, the technique cannot be used to index large number of grains due to the large margins required since the position of the diffracting grains is neglected during indexing.

4.1.3.1.3 Alternative approaches  (i) One technique involves matching the angles between all the pairs of the observed diffraction spots and a database of the allowed angles depending on the crystal structure. However, since the number of pairs scales as \(n^2\), where \(n\) is the number of diffraction spots, this method cannot be used for a large number of diffraction spots [16]. This technique is implemented in ImageD11 [12], which has been shown to work satisfactorily for up to 275 grains.

(ii) Another example is using tomography or extinction data to assign the diffrac-
4. Determination of volume, centre of mass, crystallographic orientation and strain state of grains

... spots to grains $^{[4][19]}$. However, this approach requires data acquired using high resolution detectors placed close to the specimen, which, although enable grain boundary mapping, have longer acquisition times. Furthermore, the number of grains in this technique is limited by peak overlap on the high-resolution detectors.

(iii) In a separate technique, if the number of grains in the specimen is small and the width of size distribution of grains is large, diffraction spots are assigned to grains based on the volume of grains derived from diffraction spots. An extension to this technique can be used for a larger number of grains if the evolution of grain volume as a function of time during a heat treatment (or deformation etc.) is known. Then, all the spots which show a similar evolution of grain volume over time are grouped together $^{[8]}$. However, both the methods based on grain volumes suffer from a high chance of false hits for large number of grains (since multiple grains can have the same volume / evolution of volume).

4.1.3.2 Present approach

All the techniques mentioned in §4.1.3.1 suffer from one or more drawbacks if the number of grains in the illuminated volume is large. Thus, a combination of multiple approaches is presented here. First the hypothetical case where the position of all the grains is assumed to be at $(0, 0, 0)_{lab}$ is described and then the approach is extended to include the effect of grain position in the specimen on the position of the diffraction spots.

Start with assumption that all the grains in the illuminated volume are present at $(0, 0, 0)_{lab}$. For each observed diffraction spot, the orientation of the normal to the diffracting plane is fixed. However, in order to define the full crystallographic orientation, the orientation of at least two non-parallel directions needs to be known. The more the number of known directions, the better is the accuracy of indexing. In order to determine these, the diffracting plane is rotated about the plane normal axis in pre-defined steps in order to generate all symmetrically unique crystallographic orientations for which the plane normal is aligned in the direction defined by the diffraction spot (partial backward projection). This is similar to the discretisation of the straight line in RF space into a number of orientations followed by Bernier et al. $^{[10]}$. For each of the generated orientations, diffraction spots are simulated (forward projection). The observed diffraction spots are compared with the simulated diffraction spots and the orientation with the maximum number of matched diffraction spots and the smallest mean difference
between the simulated and the observed position of the diffraction spots can be stored as a guess of orientation of the corresponding grain (the guess is refined later). Furthermore, the grain volume corresponding to all the diffraction spots to be matched should be within a pre-defined margin of grain volume corresponding to the starting diffraction spot.

In case the diffracting grain is not positioned at \((0,0,0)_{\text{lab}}\), the diffraction spots are displaced from the ideal position on the diffraction ring calculated according to \((0,0,0)_{\text{lab}}\). This is not problematic if wide margins are used during matching and the number of diffraction spots is low, such as is the case in the method of Bernier et al. [10]. However, in case the number of grains in the illuminated volume is large, a number of spots might be present within the margins during matching and thus the probability of matching with wrong diffraction spots is high. A possible method to circumvent this problem is to place the centre-of-mass of the grain at different positions on a pre-defined grid in the illuminated volume (map the position of the grain in the full specimen volume) and then trying all the orientations resulting from the rotation of the diffracting plane. However, depending on the size of the grid, this procedure is very computationally intensive, even though it is faster than forward projection due to the reduced number of orientations. Thus, an alternative (and more computationally efficient) approach is developed, in which, for each starting diffraction spot, a surface in the specimen is scanned instead of the whole illuminated volume:

Starting with a diffraction spot, its position with respect to the ideal diffraction ring for grains positioned at \((0,0,0)_{\text{lab}}\) is calculated, shown in Figure 4.3(a). A number of different combinations of the centre-of-mass position and the orientation of the diffracting grain can give rise to this observed position of the diffraction spot. Now consider a plane \(AA'\), parallel to the detector and passing through \((0,0,0)_{\text{lab}}\). Assuming that the diffracting grain was present at \((0,0,0)_{\text{lab}}\) and the orientation of the diffracting plane normal was such that the diffraction spot would be observed at point \(O_p\) on the ideal diffraction ring as shown in Figure 4.3(b), the position of the grain in plane \(AA'\) which would give the observed diffraction spot can be calculated by drawing a diffracted ray parallel to the straight line from \((0,0,0)_{\text{lab}}\) to \(O_p\). This procedure results in point \(p\) as the possible position of the grain. Similarly, if the diffraction ring is divided into a number of points, as shown in Figure 4.3(c), and the same procedure explained earlier for point \(O_p\) is carried out for each of these points, this results in an equal number of possible positions of the diffracting grain in the plane \(AA'\), each one with a different orientation of the diffracting plane normal and each one of which can give rise to the observed diffraction spot, but,
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if placed at \((0,0,0)_{\text{lab}}\), would result in a diffraction spot at one of the points on the ideal diffraction ring. Now, considering one of these points in plane \(AA'\), the diffracting grain (with fixed orientation of the diffracting plane normal) can be located not only at this point, but at any position along the diffracted ray passing through this point and the observed diffraction spot, shown in Figure 4.3(d). The combinations of all these positions in the specimen lying on diffracted rays to the observed diffraction spot and passing through the points found on the plane \(AA'\) define a surface shown in Figure 4.3(e). The surface thus calculated is divided into a grid and diffraction spots for all the combinations of positions on the grid and orientations (by rotating the diffracting plane about its normal) are simulated and matched with observed diffraction spots using margins for position on the detector, position in \(\omega\) and volume of the grain. The combination of position and orientation with the best match qualifies as belonging to the grain in question.

Figure 4.4 shows a comparison of the number of computations required in the three different modes (which can successfully be used for experiments with a large number of grains) as a function of number of grains in the illuminated volume. The three modes are:

(i) forward projection mode where all the orientations and the full specimen volume are mapped;

(ii) the mode where the number of trial orientations is reduced by taking the observed diffraction spots as starting points but scanning the whole specimen volume for each orientation and;

(iii) the mode where only a single surface per starting diffraction spot is mapped for a reduced number of orientations.

All three modes were simulated with similar step sizes in position and orientation for a cubic specimen with F.C.C. phase. Only the diffraction spots belonging to the \{200\} family of planes were chosen as starting points in the modes with reduced trial orientations because of their low multiplicity. It can be seen from Figure 4.4 that, even for 10,000 grains, the mode in which surfaces in the specimen are mapped for a reduced number of trial orientations is orders of magnitude faster than the other two modes. Any higher number of grains would pose the problem that individual diffraction peaks cannot be identified anymore and almost complete powder rings would be observed. It must be noted here that, in the case of textured / deformed materials, the limit for the maximum number of grains, which still result in individual resolvable diffraction spots, can be lower than 1000 grains.
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Figure 4.3: Schematic of the procedure to determine the search surface belonging to a diffraction spot. (a) Diffraction event from a grain gives a diffraction spot on the detector. Plane AA’ is parallel to the detector plane and passing through (0,0,0)_{lab}. (b) Illustration of a possible position of the diffracting grain (point p) in plane AA’ which can give rise to the observed diffraction spot. Straight lines from p to the observed diffraction spot and from (0,0,0)_{lab} to O_p are parallel to each other. The direction X determines orientation of the diffracting plane normal. (c) By dividing the ideal diffraction ring into a number of discrete points, the corresponding possible positions of the diffracting grain in plane AA’ are found. Each point defines a combination of the orientation of the diffracting plane normal and a position in the plane AA’. (d) Each possible position in plane AA’ determined in the previous step defines a projection of the possible position of the diffracting grain along the diffracted beam. (e) The surface (greyed area) in which the position of the centre-of-mass of the diffracting grain is searched. This surface is defined by straight lines each passing through a point in plane AA’ shown in (c) and in the direction from the point towards the observed diffraction spot (possible direction of the diffracted beam).
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Figure 4.4: Number of computations in three different modes of indexing as a function of the number of grains in the illuminated volume. The simulated specimen (F.C.C. phase) is a cube of $1000 \times 1000 \times 1000 \ \mu m^3$. The grid size in position is $5 \ \mu m$ and the step size in orientation is equivalent to rotation of the diffracting plane around the normal to the plane by $0.2^\circ$. A computation is defined as the process of simulating the diffraction spots for an orientation and a position and comparison of the simulated diffraction spots with the observed diffraction spots.

4.1.3.3 Implementation

During indexing, the procedure described in §4.1.3.2 is followed in order to determine the diffraction spots belonging to grains and the guesses for centre—of—mass position and orientation of the grains. The algorithm has been implemented in C. The program can be run in following two modes depending on number of grains in the illuminated volume and an overview of each mode is also given in Table 4.1.
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<table>
<thead>
<tr>
<th>Non−mapping mode</th>
<th>Mapping mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Only suitable for a small number of grains.</td>
<td>Suitable for a large number of grains due to the small margins that are used.</td>
</tr>
<tr>
<td>All grains are assumed to be present at ((0, 0, 0)_{\text{lab}}).</td>
<td>Position of the grains in the specimen is determined by clever mapping approach.</td>
</tr>
<tr>
<td>Large margins are required to be used.</td>
<td>Small margins can be used due to the position determination.</td>
</tr>
<tr>
<td>Computationally very fast.</td>
<td>Computationally more intensive but faster than conventional techniques.</td>
</tr>
</tbody>
</table>

Table 4.1: Overview of the features of the non−mapping and the mapping modes of indexing.

In the non−mapping mode, if the number of grains in the illuminated volume is low, the step involving the determination of the centre−of−mass position of the grains is skipped and all the grains are assumed to be present at \((0, 0, 0)_{\text{lab}}\). This way, only an initial guess for the orientation of the grains is determined. Wide margins are used during matching the simulated diffraction spots with the observed diffraction spots in order to compensate for the effect of the position of the grains. The centre−of−mass position and the orientation of the grains are then determined during refining using the procedure described in §4.1.4. The advantage of this mode is that the algorithm can be executed much faster than if position of the grains is also determined. This mode is similar to the method of Bernier et al. [10].

In the mapping mode, both the position and the orientation of the grains are determined by using the reduced orientations surface scanning method described in §4.1.3.2. This mode requires more computation time, which depends on the grid size used. However, since both the position and the orientation are determined simultaneously, the margins during matching of the simulated and the observed diffraction spots can be kept quite low. This is especially useful when the number of grains in the illuminated volume is large leading to numerous diffraction spots being present close to each other. Furthermore, due to the intrinsic nature of the present indexing approach, where all the starting diffraction spots are treated independently of each other, the implementation achieves ideal speedup for multiple processors.

4.1.3.3.1 Margins for matching position of diffraction spots  The margins used for matching the observed diffraction spots with the simulated diffraction spots
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require special attention. In order to define the margins, first the potential sources of differences in the position of the simulated and the observed diffraction spots need to be considered, which are:

(i) The uncertainty in the position of the observed diffraction spots. This emanates from the limited detector resolution, the inaccuracy in the rotation of the specimen (so-called wobble), the inaccuracy resulting from peak searching, the number of diffraction images in which a diffraction spot is observed and the accuracy in determining the global parameters. This can be estimated from the experiment.

(ii) Finite size of the scanning grid for the position of the grains in the specimen due to which the simulated diffraction spots can be off from the ideal position of the diffraction spots. This can give a maximum error equal to the grid size.

(iii) Finite angle of the rotation of the diffracting plane normal in order to generate candidate orientations. This effect is complicated since the rotation of a plane normal by an angle has varying effects on the orientation of the rest of the planes and thus the corresponding position of the diffraction spots.

In view of the sources of the differences in the position of the simulated and the observed diffraction spots, the margins are defined as follows:

(i) The margin in $\omega$ is divided into two parts: the uncertainty in the position of the observed diffraction spots in $\omega$ and the effect of rotation of the diffracting plane normal. The latter is also a function of $\eta$.

(ii) The margin in the position on the detector is also divided into two parts: the uncertainty perpendicular to $\eta$ and the uncertainty along $\eta$. The uncertainty in the radial direction perpendicular to $\eta$ is only dependent on the experimental inaccuracy and the size of the grid during mapping. The uncertainty along $\eta$ depends both on the experimental inaccuracy and on the angle of rotation of the diffracting plane normal.

The program requires only the experimental inaccuracies as input while the effect of rotation of the diffracting plane normal is calculated automatically. In the present implementation, a so-called ‘maximum uncertainty approach’ is followed, in which the margins due to the rotation of the diffracting plane normal are calculated based on the maximum uncertainty, which can be present, in order to minimize the computation overhead. The uncertainty along $\eta$ (±) corresponding to the rotation of the diffracting plane normal is taken as equal to half of the angle of
4.1. Indexing using a surface scanning technique

rotation of the diffracting plane normal \((0.5\Delta R_{\text{normal}})\). The uncertainty in \(\omega\) \((\pm)\) corresponding to the rotation of the diffracting plane normal is taken as equal to \((0.5\Delta R_{\text{normal}}/|\sin \eta|)\).

4.1.3.3.2 Speedup during position mapping  As shown in Figure 4.4, the mapping mode with reduced orientation and sample surface mapping is multiple orders of magnitude faster than all orientations and full sample mapping. However, in practice, even \(\sim 10^{11}\) computations for around 7000 grains can be computationally prohibitive, especially since each ‘computation’ itself encompasses calculation of diffraction spots according to a position and orientation of the grain and comparison with the observed diffraction spots. Thus, during indexing, two limiting steps can be identified:

(i) The number of observed diffraction spots compared with each calculated diffraction spot: Within a single ‘computation’, the observed diffraction spots are compared with each calculated diffraction spots and if not optimized wisely, this can lead to considerable reduction in the efficiency of the programs. The simplest, and computationally slowest, way is to compare all the observed diffraction spots with each calculated diffraction spot and find all the matches, which lie within the margins. However, given that the total number of diffraction spots during a ‘typical’ 3DXRD experiment can be \(\sim 100,000\) (for 1000 grains and \(\omega\in [-180^\circ; 180^\circ]\)); this would lead to very slow execution of the program. In the first level of optimization, only the spots, which have \(\omega\) – values within the chosen \(\omega\) – margins, can be compared. This already reduces the number of observed diffraction spots being compared with each calculated diffraction spot to \(\sim 1000\), a speedup of 100 times. Furthermore, a second filtering step of comparing only the spots belonging to the diffraction ring corresponding to the calculated diffraction spots is applied. Depending on the multiplicity \((m_{hkl})\) of the diffraction ring, this can give an overall speedup of up to four times in case the total number of diffraction rings is four. The total number of observed diffraction spots being compared with each calculated diffraction spot is then reduced to \(\sim 250\).

The next step is to filter the observed diffraction spots based on the chosen margins along \(\eta\). This further reduces the total number of observed diffraction spots to be compared with each calculated diffraction spot from \(\sim 250\) to \(\sim 4\). The last filter is to compare with only those observed diffraction spots, which lie within the chosen radial margins perpendicular to \(\eta\). The number of observed diffraction spots to be compared with a calculated diffraction spot is then a maximum of two
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and, in most cases, zero. The filtered observed diffraction spots are pre–calculated, that is, look–up tables consisting of the information about the observed diffraction spots to be compared are generated for discretized possible positions of calculated diffraction spots on a small grid. *GrainSpotter*\(^4\) \([12,13]\) also uses look–up tables in order to achieve computational speedup. The typical sizes of the grid are: 0.3° in \(\omega\), angles equivalent to 50 \(\mu\)m in \(\eta\) (different for each diffraction ring) and 50 \(\mu\)m in the radial direction perpendicular to \(\eta\). The optimization by reducing the number of observed diffraction spots from all the spots within the \(\omega\)–margins to only the spots within all the chosen margins (in \(\omega\), along \(\eta\) and perpendicular to \(\eta\)) and the generation of look–up tables has been found to yield a speedup in the indexing time of \(\sim\)500 times (for a dataset consisting of a total of 300,000 diffraction spots and 3000 grains).

(iii) The total number of ‘computations’ required: this scales with the number of starting diffraction spots, which is directly proportional to the number of grains in the illuminated volume, the number of symmetrically unique orientations generated and the size of the grid on the search surface. Out of these three, the first parameter, *i.e.*, the number of starting diffraction spots, can be minimized by choosing only 2–3 diffraction spots per grain, instead of all the diffraction spots. Choosing a single diffraction spot per grain as a starting spot is not a good choice due to the possible problems associated with diffraction spots, which were not successfully fit during peak characterization.

The second parameter to reduce the total number of computations required, is the number of symmetrically unique orientations and can either be reduced by increasing the angle over which the diffracting plane is rotated, which increases the associated margins (as described in the previous section) and thus not recommended, or by choosing starting diffraction spots belonging to family of planes with the highest symmetry (only works for cubic structures). For example, for a fixed rotation angle of the diffracting plane, a plane belonging to the fourth diffraction ring \{311\} for F.C.C. has four times higher number of symmetrically unique orientations as compared to a plane belonging to the second diffraction ring \{200\}.

The third parameter, which directly affects the total number of computations required, is the size of the grid on the surface and which can, in its simplest form, be increased in order to reduce the total number of computations required. However, a coarser grid on the search surface has the detrimental effect of higher (possible) errors in the centre–of–mass position (and, to a lesser extent, orientation) of the

\[http://sourceforge.net/apps/trac/fable/wiki/grainspotter\]
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grains after indexing. In order to arrive at a solution, first consider Figure 4.5, which shows the maximum fraction of diffraction spots matched as a function of position along a single diffracted ray (described in Figure 4.3) on the search surface for an example simulation with 3000 grains in the illuminated volume. The maximum fraction is the maximum of the number of simulated (observed) diffraction spots matched with the calculated diffraction spots divided by the total number of calculated diffraction spots (100 in this case) for all the symmetrically unique orientations and a fixed position along the diffracted ray. The number of observed diffraction spots matched with the calculated diffraction spots increases as the number of grains in the illuminated volume and/or the margins chosen during indexing are increased.

It can be seen from Figure 4.5 that, except for positions between \( \sim 425 \ \mu m \) to \( \sim 625 \ \mu m \), the fraction of diffraction spots matched is lower than 0.4. The real position of the grain in question was 516 \( \mu m \). Plots similar to Figure 4.5 can also be made for the other dimension of the grid on the search surface. Considering the (relatively) large numbers of positions for which the fraction of the matched diffraction spots is lower than 0.4 as compared to the number of positions for which the fraction of the matched diffraction spots is greater than 0.4, an adaptive grid is employed during indexing: for a certain position \( P \), if the maximum fraction of the matched diffraction spots is lower than 0.5 times the minimum fraction used to define the successful detection of a grain, a number of the points following the position \( P \) on the grid are skipped. The number of points, which are skipped, \( N_{\text{skip}} \), is calculated as:

\[
N_{\text{skip}} = N_{\text{skip}_{\text{max}}} - \text{int} \left( \frac{F_{\text{max}}}{0.5 F_{\text{accept}}} \left( N_{\text{skip}_{\text{max}}} - 1 \right) \right) \tag{4.9}
\]

where, \( F_{\text{max}} \) is the maximum fraction of diffraction spots matched at the present position on the grid, \( F_{\text{accept}} \) is the minimum fraction of diffraction spots matched used to define the successful detection of a grain and \( N_{\text{skip}_{\text{max}}} \) is the maximum number of grid points, which are skipped. Equation 4.9 shows that 1 to \( N_{\text{skip}_{\text{max}}} \) points on the grid are skipped during indexing depending on \( F_{\text{max}} \) (between 0.5\( F_{\text{accept}} \) and 0) if \( F_{\text{max}} \) is less than 0.5\( F_{\text{accept}} \). For simulations using a grid size of 5 \( \mu m \) in a cylindrical sample of 500 \( \mu m \) radius, 500 \( \mu m \) height and 3000 grains, skipping the regions with low \( F_{\text{max}} \) has been found to result in a speed–up of around 5–10 times (depending on the chosen values of the parameters in Equation 4.9 and the number of diffraction spots in the dataset) as compared to mapping the whole surface.
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Figure 4.5: Evolution of the maximum fraction of observed diffraction spots matched with the calculated diffraction spots as a function of the position along the diffracted ray described in Figure 4.3 (d) for a random simulation. The maximum fraction is the maximum number of observed diffraction spots matched with the calculate diffraction spots divided by the total number of calculated diffraction spots (100 in this case) for all the symmetrically unique orientations. The grain was present at 516 µm.

A schematic example of the variable grid for a hypothetical case with $N_{\text{skip max}} = 4$ is shown in Figure 4.6. The position of the grain is in the middle of the figure. The surface is mapped with the default step size only within a small distance around the real position of the grain. In this case, the diffracted rays are assumed parallel to the $y$–axis. In the present implementation of the code, $N_{\text{skip max}}$ is chosen to be equal to 10, whereas the step size of the grid is usually 5 µm so that the maximum distance on the surface, which can be skipped in the case of low number of matches, is 50 µm.
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Figure 4.6: Schematic illustrating the features of the adaptive grid during indexing. Each marker represents a combination of $(x, y, 0)$, which is tried as the position of the grain, where all the orientations corresponding to the rotations of the diffracting plane are tried. The grain is present somewhere in middle of the figure. Away from the real position of the grain, a number of positions on the grid are skipped ($N_{\text{skip max}} = 4$) due to the low maximum fraction of the observed diffraction spots matched with the calculated diffraction spots.

4.1.3.4 Limitations

A robust and time efficient procedure for indexing diffraction spots belonging to thousands of grains has been developed. Even so, the main limitations of the presented methodology are as follows:

(i) The procedure depends strongly on the possibility of accurate determination of global parameters. Even though there is the possibility of fitting the global parameters using the diffraction spots belonging to individual grains, it is very
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important that correct diffraction spots are assigned to grains, which, in turn, depends on the knowledge of global parameters.

(ii) The accuracy with which the diffraction data can be indexed depends on the accuracy with which the diffraction spots themselves can be characterized. This is an issue both for the position of the diffraction spots on the detector and in \( \omega \). Due to the limited spatial resolution of the detectors (\( \sim 50 \) \( \mu \)m for ‘fast-mode’ 3DXRD), the accuracy of with which the position of the diffraction spots can be determined depends on the size of the diffraction spots on the detector. If the diffraction spots are large, i.e., covering a large number of pixels (more than 20 pixels), the position of the centre-of-mass of the diffraction spots can be determined with sub-pixel accuracy. However, if the diffraction spots are only a few pixels in size (for small grains), the accuracy with which the position of the centre-of-mass of the diffraction spots can be measured is worse. Similarly, if a diffraction spot is observed only in one or two diffraction images, the uncertainty in \( \omega \) is worse than if the diffraction spot is observed in more diffraction images. This can be solved by reducing the rotation step, \( \Delta \omega \), during the experiment at the cost of time resolution, however.

(iii) In the mapping mode, the methodology presented here is computationally intensive, though not as intensive as other (hypothetical) techniques for similar numbers of grains. Since the computation time scales with the number of diffraction spots, this also means that data acquired from specimens with more grains in the illuminated volume requires longer processing time. However, the mapping mode allows for handling much larger number of grains simultaneously than the non-mapping mode, thereby allowing for better time resolution during experiments: as compared to scanning multiple layers with small number of grains, a much larger number of grains can be followed for a single layer.

4.1.4 Refinement

The experimental inaccuracy in the position of the centre-of-mass of the diffraction spots directly translates into inaccuracy in the position of the search surface calculated during indexing. Furthermore, in the non-mapping mode, the position of the grains is assumed to be at \((0,0,0)_{\text{lab}}\). Thus, the centre-of-mass position and the orientation of the grains are refined in the second part by using the diffraction spots matched during indexing. During refinement, the sum of the squared angle between the observed and the simulated scattering vectors (so-called internal
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angle\(^5\) is minimized. *GrainSpotter*\(^6\) \[12,13\] also uses internal angles for optimization. The algorithm has been implemented in MATLAB\(^\circledR\). The minimization is carried out using the *fmincon*\(^7\) function inbuilt in MATLAB\(^\circledR\). The function *MultiStart* is employed to call *fmincon* using a number of different starting guesses for orientation and centre—of—mass position of the grains. This procedure increases the probability that the optimized orientation and position of the grains are not just the local optima close to single starting values, but the global optima.

During refinement, outliers are automatically rejected based on the value of the internal angle. If the internal angle corresponding to a diffraction spot is higher than twice the mean value of internal angle for the grain, the diffraction spot is rejected as an outlier. In addition to the refinement of the centre—of—mass position and the orientation of the grains, the program iteratively checks whether all the spots matched during indexing are the best matches or not. If not, the corresponding spots (outliers) are rejected and the spots, which result in the smallest value of internal angle, are indexed with the grain. The best match is calculated based on the internal angle.

4.1.5 Strains

The treatment thus far has not included strained lattices, which affect the position of the diffraction spots, both on the detector and in \(\omega\). Mapping of the strain state of grains during indexing increases the required computation time significantly. Furthermore, as will be shown in §4.1.6.2, mapping of the strain state during indexing is not required if the experimental setup / the number of grains are adjusted properly by either reducing \(L_{sd}\) or reducing the number of grains in the specimen volume illuminated by the X-ray beam. The effect of elastic strains on the position of the diffraction spots is thus taken into account during refinement. In addition to the six parameters, which are refined for un—strained specimens: three for the position of the grains and three for the crystallographic orientation of the grains, six additional parameters defining the strained lattice: \(a, b, c, \alpha, \beta, \gamma\), are refined. The strained lattice parameters, in addition to the un—strained lattice parameter, are used to define the strain tensor in the Cartesian grain coordinate system as \[13,20\]:

\[\begin{align*}
\end{align*}\]

\(^5\)Although the internal angle is biased towards the error in \(\omega\), it is observed to have a negligible effect on refinement.

\(^6\)http://sourceforge.net/apps/trac/fable/wiki/grainspotter

\(^7\)http://www.mathworks.com/help/toolbox/optim/ug/fmincon.html
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\[ \varepsilon = \frac{1}{2} \left[ AA_0^{-1} + \left( AA_0^{-1} \right)^T \right] - I \]  \hspace{1cm} (4.10)

where \( A \) is the metric relating the direct–space coordinate system to the Cartesian grain system, given as \[21\]

\[
A = \begin{pmatrix}
a & b \cos \gamma & c \cos \beta \\
0 & b \sin \gamma & -c^* \sin \beta \cos \alpha^* \\
0 & 0 & c \sin \beta \sin \alpha^*
\end{pmatrix}
\]  \hspace{1cm} (4.11)

and \( A_0 \) is Equation \[4.11\] for the unstrained lattice and \( I \) is the identity matrix. The reciprocal lattice parameters are given as \( a^*, b^*, c^*, \alpha^*, \beta^* \) and \( \gamma^* \). The strain tensor in the sample coordinate system is then \[13\]

\[ \varepsilon_{\text{sample}} = U \varepsilon U^T \]  \hspace{1cm} (4.12)

where \( U \) is the orientation matrix for the grain. Equation \[4.12\] is only valid for the elastic deformation regime.

The normal to the plane, \( n_s \) in Equation \[4.4\] is calculated as \( n_s = B n_{hkl} \) by using the metric \( B \) relating the reciprocal space to the Cartesian grain system defined as \[21\]

\[
B = \begin{pmatrix}
a^* & b^* \cos \gamma^* & c^* \cos \beta^* \\
0 & b^* \sin \gamma^* & -c^* \sin \beta^* \cos \alpha \\
0 & 0 & c^* \sin \beta^* \sin \alpha
\end{pmatrix}
\]  \hspace{1cm} (4.13)

### 4.1.6 Test cases

All the algorithms have been tested thoroughly using simulated data, which can be used to compare the refined and the real characteristics of the grains. Two cases, one each using the non—mapping mode for low number of grains and the mapping mode for large number of grains, are described for the algorithms for un—strained samples. The algorithms for strained samples are verified using the mapping mode.
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4.1.6.1 Unstrained simulations

4.1.6.1.1 Non-mapping mode The non-mapping mode is very time efficient for indexing if the number of grains in the illuminated volume is low. Simulations were performed with PolyXSim, the FABLE polycrystal simulator. A specimen consisting of 60 grains of austenite (F.C.C., $a_0 = 3.55 \, \text{Å}$) was chosen for simulation. The grains, with random orientations and sizes, were positioned randomly in a cylindrical volume of 500 $\mu\text{m}$ radius and 300 $\mu\text{m}$ height. A virtual detector identical to the FReLoN-4M detector [22], placed at a distance of 315696 $\mu\text{m}$ from the specimen, was used in the simulations, with X-ray energy set to 88.005 keV (Pb-edge). Diffraction spots were simulated for $\omega \in [-180^\circ; 180^\circ]$. With these settings, for the first four Debye rings, between 96 to 100 diffraction spots per grain were simulated.

Using the procedure described in Chapter 3, the global parameters of the simulation were refined. Due to the low number of diffraction spots in the simulation, the refined values for the beam centre ($y_{cen}$, $z_{cen}$), specimen-to-detector distance ($L_{sd}$) and tilts of the detector ($\beta$, $\gamma$) after refinement were unsatisfactory. Thus, a diffraction experiment for a specimen with 1000 grains was simulated with the same experimental conditions as the simulated specimen with 60 grains and the data from this simulation was used to calculate the aforementioned parameters. After indexing and refinement of the orientation and the position of the grains, all the global parameters were refined again along with the orientation and the position of the grains.

The indexing program was run as follows: only the diffraction spots belonging to the $\{200\}$ family of planes were taken as the starting spots. Potential orientations were calculated for every 0.1° rotation of the diffracting plane about the normal to the plane for each starting diffraction spot. For matching the observed and the expected diffraction spots, the margins used were 0.7° and 1000 $\mu\text{m}$ in $\omega$ and position on the detector, respectively. Such high margins (more than $2 \times \Delta \omega$ and $20 \times \text{pixel size}$) are required in order to compensate for neglecting the position of the diffracting grains in the specimen during indexing. For each starting diffraction spot, only the orientations for which at least 95% of the expected diffraction spots could be matched with the observed diffraction spots using the margins were stored. From these orientations, the best orientation for the corresponding diffraction spot was calculated as the one for which the mean internal angle has the lowest value. On a computer equipped with a 3 GHz Dual-Core Intel processor, it took 4.5 s to
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complete indexing for all the starting diffraction spots. The same operation using the mapping mode with 5 µm steps in the specimen and 0.1° rotation of the plane normal took around 10 min to execute.

Using the best orientation thus calculated during indexing as a starting guess, the orientation and the position of the grains was refined. Figure 4.7 (a) shows a histogram of the number of mis-indexed spots per grain, which were later correctly indexed during refinement. Out of the 60 grains, all the diffraction spots were correctly indexed for 34 grains whereas for one grain, 14 spots, out of the expected 100 spots, were mis-indexed. However, all the diffraction spots indexed during refinement were correct. This procedure required 40 min of computation time on the same computer. The comparison of the results from refinement and the real values is shown in Figure 4.7 (b–d). Since the representation of the orientation requires at least three parameters, the difference in ω is shown in 4.7 (c) to highlight the error in orientation. It must be noted here that the errors in grain position, the differences in ω and the internal angles are lower than what is expected for real experiments where the pixel resolution of the detector and the rotation step Δω dominate the final errors.

4.1.6.1.2 Mapping mode In §4.1.6.1.1 it was shown that even for a specimen containing only 60 grains, by using the non-mapping mode, a number of diffraction spots were mis-indexed but the computation time was at least 130 times faster than mapping mode. If majority of the indexed spots are correct, the mis-indexed spots can still be successfully identified and removed during refinement without compromising the accuracy of the results. As the number of grains in the illuminated volume increases, or if the material has a strong texture, more and more spots are present within the margins and consequently the probability of mis-indexed spots increases in the non-mapping mode. On the other hand, the mapping mode is not influenced by this effect because the margins can be set to lower values. If the majority of the diffraction spots can successfully be characterized during peak searching and fitting, the global parameters determined with high accuracy (similar to the values given in Chapter 3) and the step sizes in the position and the crystallographic orientation kept small enough (∼5 µm and 0.1°), thousands of grains can be analysed.

For testing the success rate of the non-mapping mode for a large number of grains in the illuminated volume, trial simulations were performed with PolyXSim using a specimen consisting of 1000 randomly oriented and positioned grains of
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![Histograms showing analysis results]

Figure 4.7: Results of the analysis of simulated data with a specimen containing 60 grains. (a) Histogram of the number of mis-indexed spots during indexing in the non-mapping mode for each of the 60 grains. The mis-indexed spots were later successfully detected and removed during refinement. (b) Histogram of the error in position of the grains calculated as the difference between the refined position and the real position. (c) Histogram showing the mean difference in $\omega$ calculated as the mean of the absolute difference between the $\omega$ values corresponding to the diffraction spots calculated for the refined orientation and the real orientation. (d) Histogram showing the mean internal angle for the grains.

It was found that during indexing using the non-mapping mode, not even a single output for any grain was good enough to be used for refinement. The fraction of the number of mis-indexed spots as compared to the total number of expected spots was at least 0.6 per grain, while being as high as 0.95 for a few grains. This clearly highlights the limitations of the non-mapping mode for large number of grains.
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To test the algorithms in the mapping mode, simulations were performed with PolyXSim using a specimen consisting of 3000 grains of austenite (F.C.C., $a_0 = 3.55 \text{ Å}$). The grains, with random orientations and sizes, were positioned randomly in a cylindrical volume of 500 µm radius and 500 µm height. Again, FReLoN−4M was used as a virtual detector placed at a distance of 315696 µm from the specimen and X-ray energy was set to 88.005keV. Wedge (deviation of the axis of rotation from the ideal axis of rotation orthogonal to the X-ray beam) angle of 0.1° was used. Diffraction spots were simulated for $\omega \in [-180°; 180°]$.

The simulations were divided into two cases: first one to simulate the ideal diffraction spots to validate the algorithms (un-displaced dataset) and the second one to mimic experimental conditions to judge the effectiveness of the algorithms for experiments (displaced dataset). In the latter, the position of the diffraction spots was displaced randomly by up to 25 µm (0.5 pixels) and 0.15° ($\Delta \omega/2$ for typical experiments) on the detector and in $\omega$, respectively, using a Gaussian distribution to simulate a ‘worst case scenario’ in the case of peaks that might appear in a single pixel on a single diffraction image. Furthermore, all the diffraction spots, which would have been impossible to separate during peak searching and fitting (closer than four pixels in position on the detector and 0.6° in $\omega$), were merged. This resulted in almost 5% of the total number of spots being merged and the spots that overlapped with each other were considered as a single spot.

Again, the global parameters of the experiment were refined using the procedure described in Chapter\[3]. Due to the very large number of diffraction spots in both the cases, almost 300,000 spots (≈100 per grain), the global parameters could be determined with very high accuracy and, unlike the previous case described in §4.1.6.1.1, simulation of a different specimen was not required.

The diffraction spots belonging to the \{200\} family of planes in $\omega \in [45°; 135°]$ were chosen from the un-displaced dataset as starting spots. This procedure ensures that between one to five diffraction spots per grain were chosen and a total of 8799 spots were thus identified. The corresponding diffraction spots in the displaced dataset were also chosen as starting spots for further analysis. For each chosen diffraction spot, indexing was carried out by using the step size in position for mapping the surface in the specimen of 5 µm and candidate orientations were calculated for every 0.2° rotation of the diffracting plane about its plane normal. For matching the observed and the expected diffraction spots, the margins used were 0.4° and 35 µm (0.6° and 60 µm for the displaced case) in $\omega$ and position on the detector, respectively. The margin for equivalent grain radius used was 10
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μm. Since the position of the grain in the specimen is taken into account while calculating the expected diffraction spots, the small margins could be successfully used (as compared to §4.1.6.1.1). For each starting diffraction spot, only the combinations of orientation and position for which at least 95% of the expected diffraction spots could be matched for the un–displaced case (at least 90% for the displaced case) with the observed diffraction spots using the margins were stored. From these combinations of orientation and position, the best combination for the corresponding starting diffraction spot was calculated as the one for which the mean internal angle has the lowest value. On a computer equipped with a 3 GHz Dual–Core Intel processor, it took around 12.5 hours per case (un– and displaced) to complete indexing for the 8799 starting diffraction spots.

Using the best combination of the orientation and the position of the grains thus obtained from indexing, the crystallographic orientation and the position of the grains were refined. Outliers were detected and rejected based on the criterion described in §4.1.4. In the un–displaced case, relatively few outliers were found, only 586 out of the total 297395 diffraction spots for the 3000 grains (only 414 grains had an outlier after indexing). All the correct diffraction spots were matched during refinement. All the merged spots were identified and rejected during indexing for the displaced case due to the volume criterion. Furthermore, 7235 spots (for 1843 grains) matched during indexing for the displaced case were rejected during refinement as outliers and the correct spots were identified. After refinement, all the missing spots were identified as the merged diffraction spots, the position and the integrated intensity of which were wrong. The total time taken for refinement was around 50 hours per case. The results of data analysis for both the un– and displaced data are divided into four categories:

(i) Results after indexing of the un–displaced data, hereinafter referred to as UI.

(ii) Results after refinement of the indexing results for the un–displaced data, hereinafter referred to as UR.

(iii) Results after indexing of the displaced data, hereinafter referred to as DI.

(iv) Results after refinement of the indexing results for the displaced data, hereinafter referred to as DR.

For each of the four aforementioned categories, Figure 4.8 shows a histogram of the distribution of the error in the centre–of–mass position of the grains, the mean difference in the position of the observed and calculated diffraction spots, the mean difference in Ω (directly relates to the error in orientation) and the mean.
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Figure 4.8: Results of the analysis of simulated data with a specimen containing 3000 grains. The acronyms UI, DI and, UR, DR correspond to the results obtained after indexing (I) and refinement (R) for the un-displaced (U) and the displaced data (D), respectively. (a, b) Histograms of error in position of the grains calculated as the difference between the calculated and the real position. (c, d) Histograms of the mean of the absolute difference in the detector—position of the observed diffraction spots and the position of the diffraction spots simulated using the resulting orientation and centre—of—mass position of the grains. (e, f) Histograms showing the mean difference in $\omega$ calculated as the mean of the absolute difference between the $\omega$ values corresponding to the observed diffraction spots and the diffraction spots calculated for the resulting orientation. (g, h) Histograms showing the mean internal angle for the grains.

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<table>
<thead>
<tr>
<th>Mean internal angle [°]</th>
<th>Error in grain position [µm]</th>
<th>Mean difference in the position of the diffraction spots [µm]</th>
<th>Absolute mean difference in ω [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>UI</td>
<td>0.03407</td>
<td>4.1395</td>
<td>8.4217</td>
</tr>
<tr>
<td>UR</td>
<td>0.00145</td>
<td>1.0837</td>
<td>1.9594</td>
</tr>
<tr>
<td>DI</td>
<td>0.03512</td>
<td>8.7351</td>
<td>10.7085</td>
</tr>
<tr>
<td>DR</td>
<td>0.03526</td>
<td>1.9651</td>
<td>1.7902</td>
</tr>
</tbody>
</table>

Table 4.2: Comparison of results for four different grains in the four cases (UI, UR, DI and DR) for the simulated dataset with 3000 grains. The acronyms are defined in the text.

internal angle for the 3000 grains. A first glance at the results of indexing, Figure 4.8 (a, c, e and g) and refinement, Figure 4.8 (b, d, f and h) highlights the fact that the results of refinement have lower errors than those of indexing. However, it should be noted that indexing is an essential first step to get a good estimate of the spots belonging to individual grains.

From Figure 4.8 (a, b), it can be seen that the difference between the results of un−displaced and the displaced data is not very large, even though the diffraction spots on the detector were displaced randomly by a distance up to 25 µm. This is because displacements of the diffraction spots in different directions can significantly reduce the final error in the position of the grain. On the other hand, the mean error in ω is larger for the displaced case than for the un−displaced case, Figure 4.8 (e, f), due to the very high accuracy with which wedge and a₀ were determined for the un−displaced case. These are the only two parameters in addition to the orientation of the grains and the wavelength of the X−ray beam, which affect position of diffraction spots in ω.

4.1.6.1.3 Determination of the quality of the results  Ideally, during data analysis, a single parameter should be used to determine if the results are acceptable or not. In the case of real experiments, the errors in position and orientation of the grains are two unknown parameters, knowledge of the order of magnitude of which is very important and which govern the acceptability of the results. Internal angle is a parameter, which combines both the errors in position and orientation of grains into a single value. In order to test the possibility of using the internal angle as a criterion for accepting the results of data analysis, the results of three different grains in three cases (UI, DI and DR) with similar values of internal angle are given in Table 4.2. It must be noted here that for the UR case, all the values of internal
angles were at least an order of magnitude lower than for the other three cases and are thus shown in Table 4.2 only for completeness purposes. It can be seen that even though the internal angles for the three cases are almost equal, the errors in the position of the grains and the difference in the position of the diffraction spots on the detector and in $\omega$ are not. Different combinations of errors in position and orientation of grains can yield similar values of the internal angle. Thus, the following approach is recommended:

The mean error in $\omega$ and correspondingly the error in orientation of grains can be calculated fairly easily. The only remaining unknown then is the error in the position of the grains. It can be seen from 4.8 (a–d) and Table 4.2 that, even though the values are not equal, the error in the position of the grains is of a similar order of magnitude as the mean difference in the position of the diffraction spots for all the four cases. Thus, the mean difference in the position of the diffraction spots, together with the mean error in $\omega$, parameters that can be readily determined for experiments, can be used as good criteria to determine the quality of the results.

4.1.6.2 Strained simulations

The simulation using 3000 grains in the illuminated volume, described in §4.1.6.1.2, was used to verify the algorithms dealing with the analysis of strained samples. Random strains from a Gaussian distribution with a mean $\mu=0$ and spread $\sigma=10^{-3}$ were introduced for each grain. The global parameters, determined using the simulation consisting of unstrained grains and displaced diffraction spots described in §4.1.6.1.2, were used. Furthermore, the diffraction spots were displaced randomly up to 8 $\mu$m and 0.06° in the position on the detector and in $\omega$, respectively. The displacements used in the present case are smaller than the displacements used for the displaced case described in §4.1.6.1.2 because spot broadening in deformed grains always improves the accuracy with which the position of the diffraction spots can be determined. A displacement of 8 $\mu$m in the position of the detector of a diffraction spot in the first diffraction ring for the simulation under consideration is equivalent to a displacement of 0.0015° in $2\theta$ and 0.02° in $\eta$. These displacements in $2\theta$ and $\eta$ decrease as $2\theta$ increases (for higher diffraction ring numbers). All the spots, which were too close to be successfully characterized during peak searching were merged using the same criteria described in §4.1.6.1.2.

Indexing was carried out on the 8799 spots identified in §4.1.6.1.2. For each chosen diffraction spot, indexing was carried out by using the step—size in position for mapping the surface in the sample of 5 $\mu$m and candidate orientations were
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calculated for every 0.2° rotation of the diffracting plane about its plane normal. For matching the observed and the expected diffraction spots, the margins used were 1.2° and 150 µm in ω and position on the detector, respectively and the margin for equivalent radius used was 10 µm. Higher margins, as compared to §4.1.6.1.2 for the position of the diffraction spots were warranted since unstrained state of the grains is assumed during indexing. On a computer equipped with a 3 GHz Dual-Core Intel processor, it took around 13 hours to complete indexing for the 8799 starting diffraction spots.

In the present case, a higher number of outliers were detected after indexing as compared to the cases shown in §4.1.6.1.2: 15439 outliers for the 3000 grains. This highlights the robustness of the indexing technique: on average, only 5.15 diffraction spots per grain (out of a total 96–100 diffraction spots) were mis-indexed during indexing, even though unstrained state of the grains was assumed. After indexing, the strained lattice parameter was refined along with the centre-of-mass position and the crystallographic orientation of the grains. After refinement, only 271 diffraction spots were matched with the wrong grains. On a 16-Core 2.53 GHz cluster, the total time taken for refinement was around 10 hours. As mentioned earlier in §4.1.3.3 ideal speedup was achieved using multiple processors since each grain is refined independently.

Histograms of the error in the centre-of-mass position of the grains, the mean difference in the position of the observed and the calculated diffraction spots, the mean difference in ω (equivalent to the error in grain orientation) and the mean internal angle for the 3000 grains are shown in Figure 4.9. As compared to Figure 4.8 (b, d) for the unstrained simulations, the error in grain position and the mean difference in the position of the observed and the calculated diffraction spots are higher for the strained simulation. This can be attributed to the increased number of parameters during refinement (12 parameters as compared to 6 in the case of unstrained grains), due to which the determination of the global minimum of the function being minimized during refinement is more difficult. Furthermore, independent of the results of strains analysis, it can be seen that the error in grain position and the mean difference in the position of the diffraction spots (Figure 4.9 a, b) are of the same order of magnitude, which means that, similar to §4.1.6.1.3, the mean difference in the position of the diffraction spots can be used to judge the quality of the results.

Histograms of the error in strains (tensor components ε₁₁, ε₂₂, ε₃₃, ε₁₂, ε₁₃ and ε₂₃) for the 3000 grains are shown in Figure 4.10. The mean error in the shear strain...
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Figure 4.9: Results of the analysis of the simulated data with a sample containing 3000 grains with strained crystal lattices. (a) Histogram of the error in the position of the grains calculated as the difference between the refined position and the real position. (b) Histogram showing the mean of the absolute difference in the detector–position of the observed diffraction spots and the position of the diffraction spots calculated using the refined orientation, centre–of–mass position and strain state of the grains. (c) Histogram showing the mean difference in \( \omega \) calculated as the mean of the absolute difference between the \( \omega \) values corresponding to the observed diffraction spots and the diffraction spots calculated using the refined orientation and the strain state of the grains. (d) Histogram showing the mean internal angle for the grains.

Tensor components \((\varepsilon_{12}, \varepsilon_{13}, \varepsilon_{23})\), \(5.2 \times 10^{-5}\) is about twice the mean error in the normal strain tensor components \((\varepsilon_{11}, \varepsilon_{22}, \varepsilon_{33})\), \(2.8 \times 10^{-5}\). The distributions of the errors for the six strain tensor components in Figure 4.10 can be approximated by Gaussian distributions with mean \( \mu \) equal to \(13 \times 10^{-7}, 66 \times 10^{-7}, -57 \times 10^{-7}\),
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Figure 4.10: Histogram of the errors in the strain tensor components, calculated as the difference in the refined and the real values, for the simulated data with a sample containing 3000 grains with strained crystal lattices. (a, b, c) Errors in the normal strain tensor components $\epsilon_{11}$, $\epsilon_{22}$ and $\epsilon_{33}$. (d, e, f) Errors in the shear strain tensor components $\epsilon_{12}$, $\epsilon_{13}$ and $\epsilon_{23}$. 
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\[ 8.3 \times 10^{-7}, -23 \times 10^{-7} \text{ and } 39 \times 10^{-7} \] for \( \varepsilon_{11}, \varepsilon_{22}, \varepsilon_{33}, \varepsilon_{12}, \varepsilon_{13} \) and \( \varepsilon_{23} \), respectively. The mean values of \( \mu \) for the distributions close to the ideal value of 0 show that there is no systematic bias during refinement and highlight the robustness and self-consistency of the refinement algorithms.

The effect of elastic strains on the position of the diffraction spots on the detector is not taken into account during indexing in order to keep the computation requirements low. The results presented above show that neglecting strains during indexing is not an issue even for 3000 grains and refining the lattice parameters (along with the centre-of-mass position and the orientation) after indexing suffices. This is because, for the magnitude of \( L_{sd} \) used in the simulations presented here, the displacements of the diffraction spots on the detector \( (y, z) \) due to strains within the diffracting grains (up to \( \sim 60 \, \mu m \)) are considerably smaller than the displacements of the diffraction spots due to the centre-of-mass position of the diffracting grains in the sample (up to \( \sim 500 \, \mu m \)). However, as \( L_{sd} \) is increased, the displacements in the diffraction spots on the detector due to strains increase (which also increase the sensitivity of the technique) and empirical calculations suggest that for \( L_{sd} \) more than \( \sim 600 \, \text{mm} \), and for more than \( \sim 2000 \) grains with random orientations, mapping of the lattice parameter during indexing is essential to obtain meaningful results.

4.2 Indexing using Friedel pairs

In §4.1, a novel specimen ‘surface’ scanning approach to indexing was introduced. A limitation of the technique is the computation time required for indexing, which is of the order of a number of hours to index thousands of grains. Even though this computation time is still orders of magnitude lower than the forward projection full specimen scanning approach (Figure 4.4), it still limits the application of the technique for online analysis.

The unique properties of Friedel pairs can successfully be used to improve the computation efficiency of the technique presented in §4.1. In literature, the techniques of Moscicki et al. [11] and Bernier et al. [10] already employ Friedel pairs during indexing. However, since these programs do not take the position of the diffracting grains into account and only match orientations, as explained in §4.1.3.1.2, indexing large numbers of grains poses a problem. Thus, a different approach, 9The DCT technique of Ludwig et al. [4] also uses Friedel pairs, but is different from ‘fast-mode’ 3DXRD.

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9 The DCT technique of Ludwig et al. [4] also uses Friedel pairs, but is different from ‘fast-mode’ 3DXRD.
4.2. Indexing using Friedel pairs

which accounts for both orientation and position of the diffracting grains during indexing and uses Friedel pairs for speedup, is developed.

4.2.1 Friedel pairs

Friedel pairs were introduced in Chapter 3 and a detailed description will be given here. In the 3DXRD setup for no wedge condition, if the specimen is rotated by a full $360^\circ$ in $\omega$, any plane $(hkl)$ of a grain can diffract: (i) never, if the plane normal lies inside either of two cone of half-angles equal to $\theta$ aligned with the vertical rotation axis ($\pm z$), this is the same as if the angle between the vertical axis ($\pm z$) and the plane normal is less than $\theta$; (ii) once, if the plane normal lies exactly on the surface of either of the two aforementioned cones, in other words, if the angle between the vertical axis ($\pm z$) and plane normal is exactly equal to $\theta$; (iii) twice for any other orientation of the plane normal, that is, if the angle between the vertical axis ($\pm z$) and the plane normal is greater than $\theta$. Thus, the two equivalent planes, $(hkl)$ and $(\bar{h}\bar{k}\bar{l})$, diffract a maximum of four times and the set of these four diffraction spots are called Friedel pairs.

In the diffraction geometry, Figure 4.11 (a) shows the possible orientations of the incoming and the diffracted beams corresponding to the four diffraction spots forming the Friedel pairs. The diffracting planes in this case are perpendicular to the plane of the paper. The incoming X-ray beam $D$ corresponds to the diffracted beam $A$. The other three pairs of the incoming and the diffracted beams are: $(A, D)$, $(C, B)$ and $(B, C)$. If the angle between the plane normal and the vertical rotation axis ($\pm z$) is exactly equal to 90°, that is, if the $z$-axis is perpendicular to the plane of the paper, it can be deduced from Figure 4.11 (a) that the $\omega$-rotations (counterclockwise) required to go from the condition when the diffraction spot $A$ is observed to the condition when the diffraction spots $B$, $C$ and $D$ would be observed are equal to $2\theta$, $180^\circ$ and $180^\circ + 2\theta$, respectively. For a different orientation of the diffracting plane and if the diffracting grain is positioned at $(0,0,0)_{lab}$, the four diffraction spots 1, 2, 3 and 4 in Figure 4.11 (b), shown on a single detector, have $\eta$ values equal to $\eta_{FP}$, $(-180^\circ + \eta_{FP})$, $(180^\circ - \eta_{FP})$ and $-\eta_{FP}$, respectively. The spots 1, 2, 3 and 4 in Figure 4.11 (b) correspond to diffracted beams $A$, $B$, $C$ and $D$, respectively, in Figure 4.11 (a). Since the difference in $\omega$ ($\omega_{\text{diff}}$) between the pairs (1, 3) and (2, 4) is equal to $180^\circ$, these pairs are called symmetric Friedel pairs. On the other hand, $\omega_{\text{diff}}$ between spots (1, 2) and (3, 4) is a function of $(2\theta, \eta)$ and thus these pairs are called ‘asymmetric’ Friedel pairs. $\omega_{\text{diff}}$ for asymmetric Friedel pairs,
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Figure 4.11: Characteristics of the Friedel pairs. (a) Possible directions of the incoming and the diffracted X-ray beams for two equivalent planes, \((hk\ell)\) and \(\bar{h}\bar{k}\bar{\ell}\). The beams \((A, D), (D, A), (B, C)\) and \((C, B)\) represent the four combinations of the incoming and the diffracted X-ray beams for the four spots forming the Friedel pairs. (b) The \(\eta\)–positions of the Friedel pairs are shown.
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Figure 4.12: $\omega_{\text{diff}}$ between the ‘asymmetric’ Friedel pairs as a function of $\eta$.

shown in Figure 4.12 increases as $|\sin \eta|$ decreases and as $\theta$ increases and is equal to $2\theta$ for $|\sin \eta| = 1$ (the case shown in Figure 4.11a).

The $\eta$ and the $\omega$ positions of the Friedel pairs are linked by unique properties described above. These properties can be used in multiple stages during data analysis. As explained in Chapter 3, §3.4.1 and §3.4.2, the determination of three of the global parameters of the experiment, $t_x$, wedge and $a_0$, becomes very straightforward once the Friedel pairs are identified. In the next sections, it will be shown how, depending on the $\omega$—range of the experiment, Friedel pairs can be used to improve the computation speed during indexing by two orders of magnitude as compared to the surface scanning reduced orientation indexing approach described in §4.1.
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4.2.2 Indexing using symmetric Friedel pairs

In case a symmetric Friedel pair for a diffracting grain is known, the position of the grain lies along a straight line connecting the symmetric Friedel pair passing through the specimen instead of the surface calculated in §4.1.3.2. Thus, instead of scanning the ‘surface’, only a line through the specimen needs to be mapped, leading to a substantial reduction in the number of computations. The single search line in the sample corresponding to a symmetric Friedel pair is shown schematically in Figure 4.13 (a). In case the diffracting grain is present at \((0, 0, 0)_{lab}\), the symmetric Friedel pair can be easily identified by checking for spots which are located 180° apart in \(\omega\) and are a mirror image along the \(y\)-axis in \(\eta\), e.g., spots \((1, 3)\) and \((2, 4)\) in Figure 4.11 (b). However, in real specimens, the diffracting grains are not present at \((0, 0, 0)_{lab}\). Thus, the following approach is developed:

In the following treatment, the specimen is assumed as stationary and instead the synchrotron setup is rotated. In Figure 4.13 (b), if the starting diffraction spot is located at the point \(O\) on the detector, the surface on the specimen can be calculated according to the procedure mentioned in §4.1.3.2. If this surface is back projected at the detector located on the opposite side of the specimen, the intersection results in a curve from the point \(P'\) to the point \(Q'\) as shown in Figure 4.13 (b). The points \(P'\) and \(Q'\) correspond to the orientations \(P\) and \(Q\), respectively, of the diffracting plane normal if the grain was positioned at \((0, 0, 0)_{lab}\). During the rotation of the specimen (or the synchrotron setup in this case) over 180° in \(\omega\), the position of a grain located at \((x, y, z)_{lab}\) changes to \((-x, -y, -z)_{lab}\). Thus, the displacement of the diffraction spot on the detector with respect to the ideal spot position (calculated for grains positioned at \((0, 0, 0)_{lab}\), remains the same in \(z\) while inverting in \(y\) between the symmetric Friedel pair. This is shown schematically in Figure 4.13 (c) where the symmetric Friedel pairs on a single detector are shown. For the projection of the plane normal with the two orientations at the points \(P\) and \(Q\), the corresponding position of the symmetric Friedel pairs would be points \(P_{FP}\) and \(Q_{FP}\), respectively. Displacing the points \(P_{FP}\) and \(Q_{FP}\) by the corresponding distance \((-y, z)\) as the distance between the points \(P, Q\) and the starting point \(O\), respectively, the points \(P'\) and \(Q'\) can be determined. A local search in a thin strip around the curve (in detector position and in \(\omega\)) from points \(P'\) and \(Q'\) is used to find all the spots which can be the symmetric Friedel pair of the starting point \(O\). As the number of grains in the illuminated volume increases, more and more diffraction spots will lie within the strip used for the local search. For each candidate symmetric Friedel pair, a single straight line through the specimen fixes
4.2. Indexing using Friedel pairs

Figure 4.13: Schematic of the procedure to determine the position of the symmetric Friedel pair. (a) In case the symmetric Friedel pair is known (points O and O'), the thick line connecting the symmetric Friedel pair and passing through the specimen determines the possible position of the diffracting grain. (b) The possible positions of the corresponding symmetric Friedel pairs for the starting point O are fixed by the projection of the search surface on the 'rotated' detector (thick dashed line through points P' and Q'). Symmetric Friedel pairs for a plane normal with the orientation P (or Q) will be located at point P' (or Q'). (c) The symmetric Friedel pair is shown on the detector. The points $P_{FP}$ and $Q_{FP}$ are calculated using the points P and Q. The points P' and Q' are calculated by displacing the points $P_{FP}$ and $Q_{FP}$ by the corresponding displacement in ($-y, z$).
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the possible positions of the diffracting grain. The detection of the symmetric Friedel pair does not help, however, in the number of orientations that have to be tried. This is because, even though, a symmetric Friedel pair fixes the direction of the diffracting plane normal, the in-plane rotation cannot be determined.

The approach described here is very robust in terms of computation time. In the case of the multipurpose furnace described in Chapter 2, this approach has proved to be very effective. An example of the robustness of this approach in case of experiments will be shown in §4.2.4.2. It requires, however, acquisition strategies involving rotation of the specimen over large $\omega -$ ranges (greater than $180^\circ$). In addition to the longer data acquisition times associated with such experiments, constraints arising out of the experimental setup may sometimes dictate the $\omega -$ range to be much smaller. Thus, for such cases (and in cases where a symmetric Friedel pair cannot be detected), a separate technique employing asymmetric Friedel pairs is developed and described in the next section.

In light of the aforementioned limitation, it must be noted here that symmetric Friedel pairs are indispensable for determination of two of the global parameters $t_x$ and wedge, as described in Chapter 3 §3.4.1 and §3.4.2 Thus, in cases where the experimental setup allows for a ‘front’ and a ‘back’ view of the specimen, it is highly recommended to acquire data with the symmetric Friedel pairs at least once, even if this is achieved at the cost of acquisition time.

4.2.3 Indexing using asymmetric Friedel pairs

It can be deduced from Figure 4.12 that for $\omega -$ ranges greater than $45^\circ$, most of the diffraction spots will have a corresponding spot for the asymmetric Friedel pair. The detection of the asymmetric Friedel pairs is more complicated than the symmetric Friedel pairs due to the following two reasons: (i) the difference in $\omega$ between the asymmetric Friedel pairs, $\omega_{\text{diff}}$, is a function of $(2\theta, \eta)$ as described in §4.2.1 and Figure 4.12 due to which the $\eta$ position of the diffraction spots needs to be corrected for the position of the diffracting grains and; (ii) the projection of the ‘surface’ in the specimen on the detector after rotation by $\omega_{\text{diff}}$ is no longer a curve (as is the case for symmetric Friedel pairs), but an area, shown in Figure 4.14(a, b). Thus, the following approach is followed:

The position of a possible diffraction spot belonging to the asymmetric Friedel pair is calculated for each point on the grid in the surface determined using the

10Higher values of $\omega -$ range mean better accuracy of grain positioning.
4.2. Indexing using Friedel pairs

**Figure 4.14:** Procedure for the determination of asymmetric Friedel pairs. (a) Schematic showing the projection of the search surface on the detector (red shaded region). This surface defines the possible location of the second spot belonging to the asymmetric Friedel pair. (b) For the asymmetric Friedel pair of points $O$ and $O'$, the orientation of the ideal plane normal is characterised by the points $P$ and $P'$. (c) Possible positions of the diffracting grain for the observed diffraction spot $O$ and the orientation of the diffracting plane normal $P$. 
procedure described in §4.1.3.2. All these positions taken together define the red shaded area in Figure 4.14 (a). Each position thus calculated is compared with the observed diffraction spots and all the unique matches\(^\text{11}\) are stored as a candidate. For each unique possible asymmetric Friedel pair, defined by the starting diffraction spot and a candidate, the orientation of the diffracting plane normal is fixed. For the case shown in Figure 4.14 (b), the orientation of the diffracting plane normal for the diffraction spot \(O\) is given by the point \(P\). The only possible position of the diffracting grain is then located on the diffracted ray passing through the sample to the point \(O\) and parallel to a straight line connecting \((0, 0, 0)_{\text{lab}}\) and \(P\). Thus, for each set of possible asymmetric Friedel pairs, the diffracting grain can lie along a straight line only.

In the case of an ideal setup, position of the two diffraction spots forming the asymmetric Friedel pair is enough to define the exact position of the diffracting grain. However, in case of inaccuracies in the position of the diffraction spots and due to small \(2\theta\) angles normally associated with experiments using high-energy X-rays, the error in position would be very large if only the asymmetric Friedel pair is used to define the complete position \((x, y, z)_{\text{grain}}\) of the diffracting grains. Thus, in the approach described above, the position of the diffracting grain is still mapped along the diffracted ray and only the position of the diffracted ray is determined using the asymmetric Friedel pairs.

### 4.2.4 Results

Similar to Figure 4.4, the number of computations required for the three modes of indexing described in §4.1.3.2 are plotted along with the indexing mode using either symmetric or asymmetric Friedel pairs as a function of the number of grains in the illuminated volume in Figure 4.15. It can be seen that the number of computations for the mode, which uses a reduced number of orientations and detects the Friedel pairs to reduce the number of possible positions of the diffraacting grains in the specimen, is orders of magnitude lower than the other three modes.

#### 4.2.4.1 Simulations

For the un-displaced simulation of 3000 grains described in §4.1.6.2, the computation time for indexing using the surface scanning method, \(0.2^\circ\) rotation of the diffracting plane normal, \(5 \mu\text{m}\) size of the grid on the surface and the 8779 starting positions.

\(^{11}\)Located within the user-defined margins.
4.2. Indexing using Friedel pairs

Figure 4.15: Number of computations in four different modes of indexing as a function of the number of grains in the illuminated volume. The simulated specimen (F.C.C. phase) is a cube of $1000 \times 1000 \times 1000 \mu m^3$. The grid size in position is $5 \mu m$ and the step size in orientation is equivalent to rotation of the diffracting plane around the normal to the plane by $0.2^\circ$. A computation is defined as the process of simulating the diffraction spots for an orientation and a position and comparison of the simulated diffraction spots with the observed diffraction spots.

Diffraction spots belonging to the $\{200\}$ family of planes in $\omega \in [45^\circ; 135^\circ]$, was 12.5 h. Using the same settings, but switching on the detection of the Friedel pairs, both symmetric and asymmetric, indexing required only 19.5 min, a speedup of around 40 times. As compared to the ideal speedup of around 250 times predicted in Figure 4.15, the speedup achieved is lower because the surface mapping approach is already optimized by skipping regions on the surface according to the maximum fraction of observed diffraction spots matched with the calculated diffraction spots (described in §4.1.3.3.2). On average, around 2 Friedel pairs were detected per starting diffraction spot.
4. Determination of volume, centre of mass, crystallographic orientation and strain state of grains

4.2.4.2 3DXRD Experiment

The 3DXRD experiment was carried out at beamline ID11 of the ESRF. A specimen of Fe−2wt% Mn was placed in the multipurpose furnace described in Chapter 2, heated to a temperature of 1100 °C, held isothermally for 3 h and cooled to room temperature at a rate of 2 °C/min. The X-ray beam, 500 µm high and 1200 µm wide, was calibrated to the energy of 88.005 keV (Pt−edge) using a Laue−Laue setup. In order to reconstruct the (partial)−3D microstructure of the specimen, a FReLoN−4M detector [22] with 2048 × 2048 pixels of 50 × 50 µm pixel size was placed at a distance of ∼375 mm from the specimen. Diffraction images were acquired for \( \omega \in [-130.05°; 46.95°] \cup [49.95°; 133.35°] \) in 0.3° steps. This \( \omega \)−range was chosen in order to comply with the requirements of the 3DXRD furnace described in Chapter 2. With this setup, the first three Debye−Scherrer rings for the ferrite phase (B.C.C.) are completely visible on the detector. A total of 560 diffraction images were thus recorded.

After pre−processing of the diffraction images and determination of the global parameters, indexing was run using the following parameters: diffraction spots belonging to the \{200\} family of planes in \( \omega \in [50°; 130°] \) taken as starting spots, 5 µm step of the grid in the surface, 0.2° rotation of the diffraction plane normal, 60 µm and 0.4° margins in position on the detector and in \( \omega \), respectively, and detection of the symmetric and the asymmetric Friedel pairs enabled. The total time taken for indexing and refinement on a computer equipped with a 3.0 GHz Dual−Core Intel processor was 18 min and 26 h, respectively. Because multiple diffraction spots from the same grain were chosen as starting spots, individual grains were sorted as follows:

Using the results of refinement, all the individual results for which a minimum of 75% of the matched diffraction spots were the same were clubbed together, so called intermediate grains. For each pair of dissimilar spots, the spot, which resulted in the smallest internal angle, was chosen as belonging to the grain in question. Afterwards, a search of diffraction spots assigned to multiple intermediate grains was carried out. Each spot assigned more than once was reassigned to the intermediate grain for which it resulted in the smallest internal angle. Indexing, refinement and the aforementioned procedure were carried out again on all the spots not assigned to any grain. Refinements of the centre−of−mass position and the orientation of all the intermediate grains were carried out once more. In each step, if the mean error in \( \omega \), the mean difference in the position of the observed and the simulated diffraction spots increased to values more than 0.07° or 29 µm,
Figure 4.16: Centre-of-mass position of the 2281 indexed ferrite (B.C.C.) grains in the illuminated volume. The axis values are in µm. The illuminated volume was a cylinder of 1000 µm diameter (x, y) and 500 µm height (z). The position of each marker represents the centre-of-mass of a grain, the colour of each marker corresponds to the orientation of the grain according to the colour legend on top right and the size of each marker is equal to the radius of the corresponding grain divided by a factor of approximately 3 in order to visualize the grains.
4. Determination of volume, centre of mass, crystallographic orientation and strain state of grains

respectively, or if the fraction of matched to expected diffraction spots dropped below 0.8, the grain was rejected. This step took a total of 159 min to process.

In the end, more than 91% (corresponding to 96.2% of the illuminated volume) of the diffraction spots were successfully assigned to 2281 grains. The rest 9% can be attributed to either (i) very small grains for which only a few spots can be detected or; (ii) overlapping diffraction spots, which were too close to be successfully resolved. The reconstruction of the (partial−) 3D microstructure of the illuminated volume of the sample is shown in Figure 4.16. The position of each marker in Figure 4.16 corresponds to the refined centre−of−mass position of the corresponding grain whereas the size and the colour of each marker correspond to the radius (divided by a factor of approximately 3 in order to visualize the microstructure) and the crystallographic orientation of the corresponding grain. Although the dimensions of the specimen were fixed to twice the real dimensions during indexing and refinement, the outline of the volume illuminated by the X−ray beam can be seen (cylinder of 1000 µm diameter and 500 µm height) in Figure 4.16. This highlights that all the grains are placed inside the specimen, not due to constraints of the specimen size, but due to the results of minimization. It must be noted here that even though the methods of Bernier et al. [10] and Schmidt (GrainSpotter) [12] claim to be applicable for aggregates of up to 1000 grains, Figure 4.16 is the first published centre−of−mass plot of a real specimen using data acquired from thousands of grains simultaneously in a single layer.12

4.3 Summary

A robust methodology for the analysis of diffraction data acquired from specimens containing a large number of grains using high−energy high−intensity X−rays is presented. The methodology consists of two stages: indexing and refinement. The indexing methodology has two salient features: (i) the number of possible positions of the diffracting grain in the specimen is reduced by employing a novel ‘surface’ scanning approach and; (ii) the number of search orientations is reduced by taking the orientation of the diffracting plane normal into account. In comparison to the presently available indexing techniques, the indexing approach is both robust and computationally efficient for indexing more than 3000 grains. The methodology has been validated using simulated data consisting of aggregates of 3000 grains and consistent results with high accuracy of grain properties have been achieved.

12As mentioned before, the DCT technique of Ludwig et al. [4] can process up to 2500 grains, but is a different technique.
In order to achieve significant computational speedup, the indexing methodology is extended to the use of both symmetric and asymmetric Friedel pairs. For the case of simulation of 3000 grains, a speedup of around 40 times as compared to the ‘surface’ scanning approach is achieved. Even in the cases where rotation angles might be limited, asymmetric Friedel pairs can be used.

The indexing and refinement routines have been used to determine the centre−of−mass position of 2281 grains in a specimen. This large number of grains, which were successfully indexed, highlights the strengths of the technique. The methodology presented here will aid in improving time resolution of in−situ experiments due to the much higher number of grains which can be analysed simultaneously than was earlier possible.

All the algorithms developed in the present work are available online at [https://sourceforge.net/projects/short3dxrd](https://sourceforge.net/projects/short3dxrd).

### 4.4 Bibliography


4. Determination of volume, centre of mass, crystallographic orientation and strain state of grains


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Observation of Changing Crystal Orientations During Grain Coarsening

Abstract

Understanding the underlying mechanisms of grain coarsening is important to control the properties of metals, which strongly depend on the microstructure that forms during the production process or use at high temperature. Grain coarsening of austenite (\(\gamma\)) at 1000 °C in a binary Fe–2wt% Mn alloy was studied using synchrotron radiation. The evolution of volume, average crystallographic orientation and mosaicity of more than 2000 individual \(\gamma\) grains was tracked during annealing. It was found that there exists an approximately linear relationship between grain size and mosaicity, which means that orientation gradients are present in the grains. The orientation gradients remain constant during coarsening and consequently the character of grain boundaries changes during coarsening, affecting the coarsening rate. Furthermore, changes in the average orientation of grains during coarsening were observed. The changes could be understood by taking the observed orientation gradients and anisotropic movement of grain boundaries into account. Five basic modes of grain coarsening were deduced from the measurements which include: anisotropic (I) and isotropic (II) growth (or shrinkage); movement of grain
boundaries resulting in no change in volume but change in shape (III), movement of grain boundaries resulting in no change in volume and mosaicity, but change in crystallographic orientation (IV); and no movement of grain boundaries (V).

5.1 Introduction

At high temperatures, coarsening of grains occurs in order to reduce the total energy of the system \([1]\). Understanding grain coarsening in three-dimensional (3D) structures is essential for control of microstructures of metals and ceramics, which bears a direct influence on the resulting mechanical and functional properties. For example, control of the grain size at high temperatures is very important for maintaining high strength of materials over time during operation in energy conversion systems.

For many decades, extensive effort has been devoted to understanding and prediction of grain coarsening at high temperatures. However, even for very simple systems, knowledge of the process of grain coarsening is still incomplete \([2, 3]\). A substantial part of the work has focused on the development of models for prediction of grain coarsening \([3, 4, 5, 6, 7, 8]\). These models assume grains as perfect crystals, the character of which does not change during coarsening and attribute coarsening entirely to the reduction of total interface area of the system \([9]\), but cannot yet accurately reproduce the real material behaviour \([1]\).

Classically grain coarsening at high temperatures in polycrystalline materials is attributed to reduction of the grain boundary area and consequently of the total energy of the system. A widely used semi-empirical grain coarsening equation to fit the experimental data for average grain sizes is expressed as

\[
D^n = D_0^n + k t
\]  

(5.1)

where \(D\) is the average grain size at time \(t\), \(D_0\) is the average grain size at the start of isothermal annealing \((t = 0)\) and \(k\) and \(n\) are empirical fitting parameters \([1]\). In most studies, values of \(n\) are commonly found to be much higher than the ideal value of 2, which is based on proportionality of the local grain curvature driving coarsening and the grain size \([1]\). A higher value of \(n\) means that the rate of grain coarsening decays faster than if \(n\) had a lower value. This effect is commonly attributed to solute drag \((i. e.,\) slowing down of grain boundaries by foreign atoms present in the matrix), to non-regular microstructures or to presence...
of texture [1], but no underpinning observations for these assumptions have been presented. More recently, a model based on stagnation of grain coarsening induced by grain–boundary smoothening has been proposed [3]. In the present chapter, an additional contribution to the oft–observed fast decay of the rate of grain coarsening is presented.

Even though significant advances have been made in modelling of coarsening, direct experimental observation of the coarsening process is lacking. Direct experimental observation of grain coarsening at high temperature requires a combination of experimental settings that, until recently, had not been accomplished: in–situ observations of three–dimensional (3D) grain volumes in the bulk of the material during coarsening. Up to date, experimental studies have been limited to ex–situ observations on cross–sections of quenched materials [10] or in–situ observations on the surface of specimens at high temperature [11]. In the first approach, the time resolution and the accuracy of the observations was limited, especially if the microstructure (e.g. γ in steel) underwent a phase transformation upon cooling. In the latter case, coarsening at the surface was studied, which can essentially differ from the bulk behaviour [12]. In either case, just a 2D analysis of the grain size distribution was performed.

The recent advances made at 3rd generation synchrotron sources capable of generating high energy X–rays with increased flux have made it possible to observe the bulk of materials [13] and study individual grains in polycrystals [14,15,16,17,18]. In a promising study, Schmidt et al. [19] studied grain coarsening in an aluminium alloy by employing the 3DXRD technique [20]. However, in the case of alloys which undergo a phase transformation upon cooling to room temperature, the technique of interrupted heat treatments as followed by Schmidt et al. [19] cannot be used. In the present chapter, the first in–situ three–dimensional observations of bulk grain coarsening at high temperatures in an alloy that undergoes a phase transformation upon cooling are presented. It will be shown that experimental observations at the level of individual grains reveal essential information about the behaviour of grains during coarsening.

5.2 Experimental details

5.2.1 Specimen

The alloy under investigation was manufactured from electrolytic (99.999% purity) iron and manganese to get a composition of Fe–2wt% Mn. The concentration of
other impurities was kept very low in order to minimize any influence of other solute particles on the rate of grain coarsening. The composition was chosen in order to slow down the rate of grain coarsening by solute drag as compared to pure iron. This was warranted by time resolution of the 3DXRD technique used. The initial material was homogenized at 1280 °C for 21 days followed by furnace cooling to room temperature. The specimen was manufactured using electro discharge machining (EDM) with dimensions shown in Figure 5.1 in order to fit in the furnace described in Chapter 2 and Reference [21]. The specimen had a change in diameter from 1 mm to 1.5 mm in the middle, which was used to define a reference by scanning with the X-ray beam.

5.2.2 3DXRD experiment

The experiment was carried out at beamline ID11 of European Synchrotron Radiation Facility (ESRF), Grenoble, France. Figure 5.2 shows the experimental setup. The specimen was placed in a furnace developed especially for 3DXRD measurements, described in Chapter 2 and Reference [21]. An S-type thermocouple was spot-welded to the top of the specimen for accurate temperature control. The specimen chamber was purged with helium and sealed at a pressure of 0.4 atm. The X-ray beam, 500 µm high and 1200 µm wide, with energy equal to 88.005 keV calibrated using a Pb-foil, was incident on the specimen at the location depicted in Figure 5.1. The specimen was heated rapidly to a temperature of 600 °C in 60 s, followed by isothermal holding for 900 s and heating to a temperature of 900 °C at a rate of 0.033 °C/s, followed by rapid heating in 120 s to 1000 °C. The specimen was then held isothermally at 1000 °C for 7740 s (2.15 h).

During the heat treatment, the furnace was rotated repeatedly over a total angle \( \omega \) equal to 24° (so-called sweep equal to one full rotation of 24°). Diffraction images were recorded using the FReLoN-4M detector [22] during every 0.3° rotation with an exposure time of 0.2 s. This setup means that every 180 s, a diffraction image is recorded at the same orientation of the specimen with respect to the incident beam. The specimen was then cooled to room temperature. Due to the limited number of grains in the illuminated volume, which satisfy the Bragg condition for diffraction in a certain orientation of the specimen, individual spots from individual grains were observed in the diffraction images. An example of a diffraction image is shown in Figure 5.3. The specimen to detector distance was adjusted in such a way that four complete diffraction rings of the \( \gamma \) phase (F.C.C.) were recorded. A \( \gamma \) grain of any crystallographic orientation combined with a rotation of the specimen over 24°
for the first four families of \((hkl)\)–planes would come into diffraction between 3 to 9 times. Thus, all the grains in the illuminated volume were studied in the present experiment. The small rotation angle of 24° means that spatial characteristics of the grains cannot be determined. However, this angle was chosen in order to have a good time resolution. At the beginning and end of isothermal annealing, the vertical size of the X–ray beam was increased to 600 \(\mu\text{m}\) in order to verify the diffraction spots originating from the grains situated partially in the illuminated volume.

**Figure 5.1:** Schematic geometry of the specimen. Position of the X–ray beam is highlighted. All the dimensions are in mm.
5. Observation of changing crystal orientations during grain coarsening

Figure 5.2: Schematic showing the experimental setup. The dimensions are not to scale. The angles 2θ, ω, and η are defined.
Figure 5.3: Example of a diffraction image showing $\gamma$ reflections at 1000 °C. Dark regions show pixels with positive intensity. The solid rings indicate the expected location of Debye–Scherrer rings for $\gamma$ phase at 1000 °C for the following (hkl) planes (radially outwards): {111}, {200}, {220} and {311}. The deviation of diffraction spots from the ideal location at the diffraction rings is due to the effect of positioning of the diffracting grain inside the specimen.
5. Observation of changing crystal orientations during grain coarsening

5.3 Data analysis method

5.3.1 Grain volume

After corrections for the beam current, the electronic noise and the detector imperfections, a minimum intensity threshold (200 counts corresponding to minimum detectable grain volume $\sim 35 \mu m^3$) was applied to characterize all the interconnected pixels as diffraction spots. The pixels with intensity above the threshold and overlapping in successive diffraction images with changing $\omega$ were merged and counted as a single diffraction spot.

The diffraction spots were assigned to families of $(hkl)$ planes using the Fable package\(^1\) and the position of the centre-of-mass of the spots was calculated in terms of $\eta, 2\theta$ and $\omega$ (Figure 5.2). The volume of the grains giving rise to the diffraction spots was calculated according to the expression:

$$V_g = \frac{1}{2} m_{hkl} \cos \theta V_{gauge} \frac{I_g}{k I_p} \Delta \theta$$  \hspace{1cm} (5.2)

where $m_{hkl}$ is the multiplicity of the $(hkl)$-ring, $\theta$ is the Bragg diffraction angle, $V_{gauge}$ is the volume of the specimen illuminated by the X-ray beam, $I_g$ is the integrated of the diffraction spot, $k$ is the normalization factor for $I_g$ and is equal to the number of diffraction images in which the diffraction spot is observed, $I_p$ is the powder intensity per diffraction images for the $(hkl)$-ring and $\Delta \Theta$ is the rotation of plane normal over which the diffraction spot is observed or, in other words, the change in the scattering angle due to rotation over $\Delta \omega$. $\Delta \theta$ is given by $\Delta \theta = \arcsin \left( \sin \theta \cos \Delta \omega + \cos \theta \sin \eta \sin \Delta \omega \right) - \theta$, where $\Delta \omega$ is the rotation angle of the specimen over which the diffraction spot is observed.

By using a relatively small tolerance ($\pm 3$ pixels on the detector and $\pm 0.3^\circ$ in $\omega$),\(^2\) diffraction spots from the same grain were identified in different sweeps. Furthermore, diffraction spots having similar volume (within a tolerance of 5%) and a similar evolution of volume during annealing were identified as belonging to the same grain. In this way, 97.3% of the specimen volume illuminated by the

\(^{1}\)http://sourceforge.net/apps/trac/fable/wiki

\(^{2}\)This was chosen to allow for changes in the orientation and the centre-of-mass position of the grains during coarsening. In case more than one diffraction spot was within the tolerances, the diffraction spot with the smallest angle between the scattering vectors of the original spot and the spots being compared was chosen.
5.4. Results

X-ray beam was characterized. The spots which showed an increase in intensity more than 5% of the integrated intensity upon opening of the X-ray beam were rejected as coming from the grains, which were partially illuminated by the X-ray beam.

The equivalent radius of the grains was calculated from the grain volume by assuming spherical shape of the grains.

5.3.2 Mosaicity and rotation of the average plane normal of grains

Mosaicity, defined per grain as the maximum difference in crystallographic orientation between any two regions in the grain \[23\], was calculated as the rotation of the diffracting plane normal required to produce a diffraction spot of the observed size in \(\omega\) and \(\eta\). In either \(\omega\) or \(\eta\), the mosaicity calculated is the maximum difference in orientation in a single direction of the grain.

The average mosaicity was calculated as the average mosaicity of all the grains with radius between intervals of 5 \(\mu\)m.\(^3\) The mosaicity per grain was calculated by averaging the mosaicity calculated from all the diffraction spots identified as belonging to the grain.\(^4\)

The average normal to a diffracting plane was calculated using the centre of mass of the diffraction spots belonging to the grain. The rotation of the average plane normal was then calculated by calculating the angle between the average plane normal of the spots for the first and the successive sweeps.

5.4 Results

Figure 5.4 shows the evolution of the volume-weighted-grain-size distribution \((P_v)\)\(^5\) in the specimen as a function of isothermal annealing time. It can be seen that, consistent with the general idea of grain coarsening, the fraction of the illuminated volume occupied by small grains is high in the beginning of isothermal annealing.

\(^3\)In the case of very big grains, diffraction spots in the first and the second diffraction rings are saturated and thus cannot be used for calculating the mosaicity. However, this has the disadvantage that the mosaicity of such grains is underestimated due to the problems with the background. Due to this reason, the average mosaicity was calculated only for the grains with radiuses up to 130 \(\mu\)m.

\(^4\)In this way, the mosaicity calculated is the average of maximum orientation difference in multiple directions. This was done in order to compare the mosaicity with equivalent grain radius.

\(^5\)\(P_v\) was calculated as the volume fraction of all grains in a volume interval divided by the volume of the corresponding interval.
which gradually decreases as coarsening progresses. This is reflected in Figure 5.5 where the volume—averaged grain volume (red symbols) and the number of grains in the illuminated volume (black symbols) as a function of annealing time are shown. It can be seen that as coarsening progresses, the average grain volume increases and the number of grains in the illuminated volume decreases.

The average volume of $\gamma$ grains (Figure 5.5 red symbols) increased from $1.24 \times 10^6$ $\mu$m$^3$ at $t = 0$ s to $9.08 \times 10^6$ $\mu$m$^3$ at $t = 7740$ s. The best fit (Figure 5.5 blue curve) of the average $\gamma$ grain size data to Equation 5.1 gives value of the grain coarsening exponent $n = 8.3$. This value is much higher than the reference value of 2, an observation made more often in literature [1]. During annealing, the number of
5.4. Results

Figure 5.5: Grain characteristics during isothermal annealing at 1000 °C. Evolution of the number of grains in the illuminated volume as a function of the annealing time (black circles) and evolution of the volume–averaged grain volume as a function of the annealing time (red squares). The blue curve shows the best fit to Equation 5.1.

Grains in the illuminated volume decreased from 2385 at \( t = 0 \) s to 1201 at \( t = 7740 \) s (Figure 5.5, black symbols). Out of the 2385 initial grains, 104 grains increased in volume, 283 had an eventual change in volume less than 5%, 814 grains decreased in volume by more than 5% and 1184 grains disappeared completely.

To highlight the relationship between size and mosaicity of the grains, the average mosaicity for all the grains in the illuminated volume is plotted in Figure 5.6 as a function of the equivalent grain radius (calculated from grain volume by assuming spherical grain shape). The error bars for the average mosaicity give the standard deviation of the observed mosaicity among the observed grains. Figure 5.6 shows that there exists an approximately linear relationship between mosaicity and grain radius.
For five $\gamma$ grains out of the 2385 observed grains, Figure 5.7 shows the evolution of grain volume, mosaicity and rotation of the average plane normal. It can be seen that, in comparison to the average grain coarsening behaviour shown in Figure 5.5 (red symbols), the volume evolution of individual $\gamma$ grains varies considerably. Figure 5.7 (a) shows an example of a $\gamma$ grain that grows continuously over time. The evolution of the grain is similar to the average grain coarsening behaviour shown in Figure 5.5. However, the grains shown in Figure 5.7 (b–e) exhibit a combination of the evolution of the size of the grains completely different from the evolution of the average grain size in Figure 5.5. The grain in Figure 5.7 (b) shrinks continuously; the grain in Figure 5.7 (c) witnesses rapid growth and then stabilizes in volume; the grain in Figure 5.7 (d) first grows, followed by shrinkage, and then disappears; and the grain in Figure 5.7 (e) shrinks, stabilizes in volume and then disappears.

A crucial feature of Figure 5.7 (a) is the development of mosaicity of the grain, which follows evolution of volume of the growing grain. This is consistent with the results for average mosaicity of all the grains shown in Figure 5.6. The grains shown in Figure 5.7 (b–e) exhibit the same behaviour, that is, the mosaicity of a grain follows the evolution of its volume. This shows that the direct relationship between mosaicity and size of the grains is also maintained during coarsening. Furthermore, Figure 5.7 (a–e) show that the average orientation of diffracting plane normal for the grains changes during coarsening. The information shown in Figures 5.6 and 5.7 is unique in terms of the extended insight that can be obtained into the behaviour of individual grains during coarsening.

### 5.5 Discussion

It is shown in Figures 5.6 and 5.7 that the mosaicity of a grain is directly proportional to its radius and that this relationship holds true during coarsening. The direct relationship between grain mosaicity and radius implies that crystallographic orientation gradients exist in the grains, which persist during coarsening such that, during the growth of a grain, the variations in its orientation increase. The presence of orientation spreads in well-annealed grains has been observed before in literature [24], but the present measurements of constant orientation gradients in grains during coarsening are first of their kind. This is very interesting, since even though, from a theoretical viewpoint, the presence of variations in orientations of crystals is thermodynamically unfavourable [1], the present observations show that not only are crystallographic orientation gradients present in the grains, but also that their magnitude does not reduce during coarsening, but remains constant instead.
Based on the observation of the maintenance of constant orientation gradients in the grains, a total of five different modes of grain evolution (shown in Figure 5.8 and Table 5.1) can occur:

(i) Mode I— anisotropic growth, I(a), or shrinkage, I(b), leads to an increase in the total mosaicity of the grain and a change in the average orientation.

(ii) Mode II— isotropic growth, II(a), or shrinkage, II(b), leads to an increase in the total mosaicity but the average orientation remains constant.

(iii) Mode III— combination of anisotropic growth and shrinkage result in the same volume, however, the mosaicity increases in one direction while it decreases in another direction. The average orientation changes after annealing in Mode
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Figure 5.7: The evolution of grain volume (black squares), the cumulative rotation of the average plane normal with respect to the original orientation (red diamonds) and the change in the mosaicity (green circles) of five individual γ grains during isothermal annealing at 1000 °C. Different shading colours represent regions of different modes shown in Figure 5.6. (a) Example of a γ grain, which increases in size. (b) A γ grain shrinking continuously over time. (c) Example of a γ grain, which grows first and then has constant volume. (d) Example of a γ grain, which initially grows and then shrinks to disappear. (e) Example of a γ grain, which decreases in volume, becomes stable and then shrinks to disappear. The error bars are calculated based on the error in measurement of the quantity.

III(a). Another variant, Mode III(b), of this mode is when the average orientation of the grain remains constant while the mosaicity in different direction changes.
Figure 5.8: Schematic illustration of the possible effects of grain evolution on mosaicty and average orientation of the $\gamma$ grains for the simplified case of grains having a constant orientation gradient in radial direction. Colours represent orientation. The cases of shrinkage are analogous to growth.
5. Observation of changing crystal orientations during grain coarsening

<table>
<thead>
<tr>
<th>Mode No.</th>
<th>Volume</th>
<th>Rotation of the average plane normal</th>
<th>Mosaicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>I (a)</td>
<td>+</td>
<td>$\Delta$</td>
<td>+</td>
</tr>
<tr>
<td>I (b)</td>
<td>-</td>
<td>$\Delta$</td>
<td>-</td>
</tr>
<tr>
<td>II (a)</td>
<td>+</td>
<td>$\equiv$</td>
<td>+</td>
</tr>
<tr>
<td>II (b)</td>
<td>-</td>
<td>$\equiv$</td>
<td>-</td>
</tr>
<tr>
<td>III (a)</td>
<td>$\equiv$</td>
<td>$\Delta$</td>
<td>$\pm$</td>
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<tr>
<td>III (b)</td>
<td>$\equiv$</td>
<td>$\equiv$</td>
<td>$\pm$</td>
</tr>
<tr>
<td>IV</td>
<td>$\equiv$</td>
<td>$\equiv$</td>
<td>$\equiv$</td>
</tr>
<tr>
<td>V</td>
<td>$\equiv$</td>
<td>$\equiv$</td>
<td>$\equiv$</td>
</tr>
</tbody>
</table>

Table 5.1: Features of the different modes of evolution of grains shown in Figure 5.8. The corresponding change in the grain volume, the rotation of the average plane normal and the mosaicity is listed. For rotation of the plane normal, there is no distinction between + or – and change is indicated by $\Delta$. For mosaicity, $\pm$ means increase in one direction and decrease in another direction.

(iv) Mode IV—combination of anisotropic growth and shrinkage results in the same volume and mosaicity of the grain, whereas the average orientation changes after annealing.

(v) Mode V—no movement of grain boundaries occurs. Volume, mosaicity and average orientation of the grain remain constant.

The case of shrinkage is analogous to growth and additional features of each mode are explained in Table 5.1. Different shading colours in Figure 5.7 are used to highlight the mode of evolution of the grains in different periods during annealing. An interesting case is the grain shown in Figure 5.9, the volume of which remains constant during annealing but the grain exhibits a combination of Mode III (which indicates changes in shape), Mode IV (which indicates no change in shape but change in centre—of—mass position) and Mode V (which indicates no apparent grain boundary movement). In order to highlight shape effects, the mosaicity of the grain in Figure 5.9 is calculated using a single diffraction spot such that mosaicity in only one direction is measured. Even though the total volume of the grain remains constant, local grain boundary motion combined with constant orientation gradients can lead to changes in the mosaicity and the average orientation of the grain as seen in Figure 5.9.
In literature, it has been proposed by the use of simulations that grains in nano-crystalline size range can rotate during coarsening \[25, 26\], similar to the observed change in orientation of the average diffracting plane normal for the grains in Figure 5.7. However, the grains shown in Figure 5.7 are of a much larger size (of the order of tens to hundreds of \(\mu m\) in radius) and rotation of the whole volume of these large grains during coarsening in absence of external stresses is not expected. The constant orientation gradients in the grains can be considered to explain the observed changes in average diffracting plane normal. The average orientation of a grain, if the observed constant gradients in orientation are present, is essentially the orientation of the centre-of-mass of the grain. Thus, in case of anisotropic growth (or shrinkage) of grains, when centre of mass of the grains shifts, the average orientation of grains changes as well. An extreme case
Figure 5.10: Example of a γ grain, same as the one in Figure 5.7(e), for which orientation in the beginning of isothermal annealing is completely different from orientation just before disappearing. Evolution of grain volume is shown by black squares and cumulative rotation of the average diffracting plane normal with respect to the original orientation is shown by red diamonds. The error bars of rotation of the average diffracting plane normal are equal to the mosaicity of the grain. The observed change in average orientation and the reduction in the mosaicity mean that no part of the grain remaining at 4000 s has the same orientation as any part of the grain which was present at the start of isothermal annealing. This is particularly interesting, since, in the case of an ex-situ study, if the same grain was observed at the beginning of annealing and at 4000 s into annealing, the different orientations would suggest that a new grain had nucleated.

Having established that grains at high temperatures have orientation gradients,
which remain constant during coarsening, the possible implications of the results on the process of grain coarsening are now examined. Even though the presence of orientation spreads in grains is well known \[1, 2, 24\], their influence on the process of coarsening has not been explored before.

Grain coarsening at high temperatures in polycrystalline materials occurs in order to reduce the total interface energy of the system ($\int \sigma \, dA$, with $\sigma$ the specific interfacial energy and the integration running over the grain boundary area in the microstructure). For each grain boundary, its contribution to the total interface energy of the system can be reduced either by reducing the contributing interface area, $A$, or the specific interface energy, $\sigma$. Reduction in $A$ takes place by increase of the radius of curvature of the grain boundaries, so-called capillarity-driven grain coarsening \[1\]. It has been proposed before by means of simulations that $\sigma$ can be reduced by changes in the inclination of the grain boundaries \[27\]. The average interface energy can also be reduced by direct elimination of high energy grain boundaries during grain coarsening \[9\].

The present observations show that orientation gradients are present in grains and that these gradients remain constant during coarsening. This means that, in the case of neighbouring grains, both having an orientation gradient, the movement of a grain boundary combined with the observed constant orientation gradient in all regions of the grains would change the local misorientation (difference in orientation at opposite sides of the grain boundary) across the grain boundary. This can be expected to affect the specific grain-boundary energy ($\sigma$), since it is known that $\sigma$ depends on the misorientation angle ($\theta$) between the grains constituting the grain boundary \[2\]. In simple terms, the relation between change in interface energy ($\Delta \sigma$) and the change in misorientation ($\Delta \theta$) can be written as:

$$\Delta \sigma = \left( \frac{\partial \sigma}{\partial \theta} \right) \Delta \theta$$

(5.3)

Depending on the sign and magnitude of ($\partial \sigma / \partial \theta$), Equation 5.3 can result in three cases: $\Delta \sigma = 0$, $\Delta \sigma < 0$ and $\Delta \sigma > 0$. In case $\Delta \sigma = 0$, there would be no effect on the driving force for grain coarsening, $G$, and grain coarsening would be driven only by curvature. In cases when $\Delta \sigma$ is negative, for example in the case of low-angle grain boundaries with decreasing $\Delta \theta$, this would result in a decrease in $G$, since $G$ is directly proportional to $\sigma$. This results, in turn, in additional decay of the rate of grain coarsening during the process. The motion of the grain boundary in this fashion would continue with an ever decreasing rate until the grain boundary
reaches a minimum in $\sigma$. In cases where $\Delta \sigma$ is positive, the motion of the grain boundary would lead to an increase in $\sigma$. Even though $\sigma$ increases, the total interface energy contribution of the grain boundary, $\int \sigma \, dA$, could still continue to decrease as long as the decrease in the interface area, $A$, can compensate for the increase in $\sigma$. A metastable condition would be reached when the motion of the grain boundary in any direction leads to an increase in $\int \sigma \, dA$, either by increasing $A$ or $\sigma$. Thus, for materials with a distribution of grain boundaries of multiple characters, the combined effect of the latter two cases would be a reduction in the overall rate of grain coarsening and consequently, an increase in the grain coarsening exponent, $n$. It must be noted here that \textit{in–situ} experimental measurement of $\sigma$ during coarsening is not possible with the techniques presently available.

The next step is to examine the probability of occurrence of the two cases which affect $n$. The change in misorientation due to movement of grain boundaries and the added imposition of maintenance of the orientation gradient will be of the order of a degree. This means that the grain boundaries, the energy of which is strongly dependent on the misorientation, for example, low angle tilt boundaries or special $\Sigma$–boundaries, are affected strongly by the relatively small change in misorientation. It is already known that the fraction of these special low energy grain boundaries in materials is high and increases during annealing [9, 28, 29]. Thus, a high fraction of grain boundaries in materials would always be affected by the change in misorientation resulting from maintenance of a constant orientation gradient.

5.6 Conclusions

Grain coarsening of $\gamma$ in a binary Fe–2wt% Mn alloy was studied by measuring the evolution of volume, average crystallographic orientation and mosaicity of more than 2000 individual $\gamma$ grains during annealing at 1000 °C. The following conclusions can be drawn from the measurements:

(i) For more than 2000 $\gamma$ grains, it was observed that the average mosaicity of all the grains is approximately directly proportional to the average grain size of the grains.

(ii) For individual grains, it is shown that mosaicity is directly proportional to the grain volume at all times during coarsening at 1000 °C. This means that constant orientation gradients exist in the grains which persist during coarsening.
The persistence of orientation gradients coupled with movement of grain boundaries results in changes in the grain boundary character, affecting the coarsening rate.

Changes in the average orientation of large (10–200 µm in radius) γ grains were observed during coarsening.

Five modes of grain growth are proposed: anisotropic (I) and isotropic (II) growth (or shrinkage); movement of grain boundaries resulting in no change in volume but change in shape (III) and movement of grain boundaries resulting in no change in volume and mosaicity, but in the average crystallographic orientation (IV); and no movement of grain boundaries (V).

5.7 Bibliography


5. Observation of changing crystal orientations during grain coarsening


5. Observation of changing crystal orientations during grain coarsening


Chapter 6

The role of orientation relationships during nucleation of austenite

Abstract

Nucleation of austenite ($\gamma$) grains in a high-purity Fe–C–Mn–Ti alloy during step-wise heating (2 °C/step) was studied by 3–Dimensional X–Ray Diffraction (3DXRD) microscopy. At all temperatures during the transformation, new $\gamma$ nuclei were observed to appear. The total number of $\gamma$ nuclei was almost 1.4 times the total number of ferrite ($\alpha$) grains before the transformation. A number of $\gamma$ grains in the specimen (as large as 120 $\mu$m in diameter) were consumed by other $\gamma$ grains during the phase transformation. The number of $\gamma$ nuclei per unit untransformed volume increased rapidly with increasing temperature. A fit of the classical nucleation theory to the measured nucleation rate showed that the overall $\Psi$–parameter, which represents the effects of the shape of the nucleus and the interfacial energies, was found to be similar to what has been reported before for the $\alpha \rightarrow \gamma$ phase transformation ($2.9 - 4.6 \times 10^{-8} \text{J}^3\text{m}^{-6}$). Close—to ideal Nishiyyama-Wassermann (N—W) orientation relationship (OR) was detected less frequently than close—to ideal Kurdjumov-Sachs (K—S) OR. Around 93% of the $\gamma$ nuclei had a either N—W or K—S OR with at least one of the neighbouring $\alpha$ grains. More than half of the
γ nuclei had a special OR with two or more α neighbours. It was surprising that the frequency of occurrence of γ nuclei having a special OR with three and four α neighbours was high, indicating the presence of a very special micro–texture. A high nucleation rate of α grains having special ORs with the parent γ grain during cooling coupled with minimal coarsening of the α grains is proposed as a possible mechanism of the formation of this special microstructure. The overall Ψ–parameter was sub–divided into five Ψ–parameters that are related to the nucleation of γ grains with K–S or N–W OR with four, three, two, one or no α neighbours. The γ grains having special ORs with four α neighbours have the lowest value of Ψ, followed, in order, by γ grains having special ORs with three, two and one α neighbours. This means that the nucleation rate is highest for the γ grains having special ORs with four α neighbours. The γ grains nucleating without a special OR with any of the α neighbours appear towards the end of the phase transformation, meaning the highest value of Ψ. These observations are instrumental for a complete understanding of the crucial phenomenon of nucleation during phase transformations in polycrystalline materials.

6.1 Introduction

The control of the microstructure during phase transformations is of immense importance to achieve desired properties in polycrystalline materials. Particularly in the case of steel, many studies have been carried out on ferrite (α) evolution during cooling, especially nucleation and growth, e.g., References [1, 2, 3, 4, 5]. As compared to the interest in the study of evolution of α during cooling, studies of the evolution of austenite (γ) during heating have been limited till now [6, 7, 8, 9]. However, for high temperature applications (e.g., fire resistant steels) as well as for applications where reheating is carried out (e.g., TRansformation Induced Plasticity steels, Quenching and Partitioning steels), the α → γ phase transformation is very important in order to achieve a desirable microstructure of the γ phase.

In the case of several types of nucleation sites, the total nucleation rate according to the classical nucleation theory (CNT) is given by [10]

\[ \dot{N}_{tot} = \sum_j \dot{N}_j = \sum_j N_{vj} Z_j \exp \left[ -\frac{\Delta G^*_j}{kT} \right] \frac{kT}{h} \exp \left[ -\frac{Q_D}{kT} \right] \exp \left[ -\frac{\tau_j}{t} \right] \] (6.1)

where \( \dot{N}_{tot} \) is the total nucleation rate per unit volume per unit time, \( \dot{N}_j \) is the
nucleation rate per unit volume per unit time for the \( j \)-th type of nucleation site, \( N_{v,j} \) is the density of potential nucleation sites of type \( j \), \( k \) is the Boltzmann constant, \( h \) is the Planck constant, \( Z_j \) is the Zeldovich factor, which accounts for the reduction in the equilibrium concentration of sub-critical nuclei due to the fact that some sub-critical nuclei become supercritical during nucleation and \( Q_D \) is the activation energy for atomic migration across the matrix–nucleus interface. \( \tau_j \) is the incubation time and \( t \) is the isothermal transformation time and \( T \) is the absolute temperature at which the transformation takes place. The activation energy for nucleation, \( \Delta G^* \), is the energy required to form a critical nucleus. In its general form, this energy is written as \( \Delta G^*_j = \Psi_j / \Delta g_v^2 \) (neglecting strain energy) [10]. Here, the factor \( \Psi_j \) accounts for the geometry of the nucleus, the energy of the interface(s) between the nucleus (\( \gamma \)) and the matrix (\( \alpha \)) phase and the energy of the \( \alpha - \alpha \) grain boundaries. The parameter \( \Delta g_v \) is the driving force for nucleation per unit volume of the nucleating phase, which is roughly proportional to the overheating, \( \Delta T \) for small \( \Delta T \).

Usually, Equation 6.1 is simplified by taking an effective nucleation rate and a single \( \Delta G^* \) for all types of nuclei, \( \tau \) is assumed to be negligible compared to the transformation time (\( t \)) and \( N_v \) is taken as directly proportional to \( f_\alpha \), the fraction of the matrix (\( \alpha \)) phase and Equation 6.1 is rewritten as:

\[
\dot{N}_{tot} \propto f_\alpha \frac{kT}{h} \exp \left[ -\frac{\Delta G^*}{kT} \right] \exp \left[ -\frac{Q_D}{kT} \right] 
\]

During cooling, as Offerman et al. [4] have shown, the nucleation rate of \( \alpha \) in \( \gamma \) first increases and then decreases as \( \Delta T \) (undercooling in this case) increases, *i.e.*, temperature is lowered. During heating, however, Equation 6.1 dictates that the term \( \exp \left[ -(Q_D/kT) \right] \) increase exponentially as temperature is increased. Furthermore, since the overheating, \( \Delta T \), also increases linearly with temperature above \( T_s \), the transformation start temperature, the term \( \exp \left[ -(\Delta G^*/kT) \right] \) also increases rapidly with increasing temperature. However, the density of nucleation sites (directly proportional to \( f_\alpha \)) decreases as the phase transformation progresses. Thus, during heating, the classical nucleation theory predicts that the nucleation rate, corrected for the density of the nucleation sites, should not have a maximum, but should increase rapidly with increasing temperature.

In the case of step-wise heating during the phase transformation, two distinctly different scenarios can occur. In the first case, the number of the nuclei forming at each stage during heating could increase in accordance with Equation 6.1.
On the other hand, once a few nuclei form at lower temperatures in the starting stages of the phase transformation, these nuclei might just keep on growing as the temperature is increased and no new nuclei might be formed.

An important parameter in Equation 6.1 is the $\Psi$ parameter, which includes the shape and the interface energies of the nucleus and the grain boundary energies. Knowledge of this parameter is very difficult, firstly, because the exact shape of the nucleus is not known and secondly, the energy of the interfaces between the nucleating phase and the matrix phase and the interfaces in the matrix phase being replaced can have a wide variety of values. For nucleation involving the replacement of an existing matrix interface (nucleation at a boundary, an edge or a corner), the $\Psi$ parameter is reduced if the energy of the matrix interfaces ($\alpha-\alpha$), which are replaced, is increased. It is also lowered if the energy of the forming $\gamma-\alpha$ interfaces, which are formed, is lowered.

Considering the effect of the $\Psi$ parameter on the nucleation rate (in the exponential), it becomes very important to study nucleation behaviour at different locations (corner, edge, boundary or intragranular) and with different ORs. Three works in this field from Huang and Hillert [2], Zhang et al. [5] and Lange et al. [11] have looked at these two aspects in the case of $\alpha$ nucleation during the $\gamma \rightarrow \alpha$ phase transformation. Even though Huang and Hillert [2] did not study the role of ORs between the $\alpha$ nuclei and the $\gamma$ matrix grains, they identified grain corners as the most common type of nucleation site. On the other hand, Zhang et al. [5] found that a much fewer fraction of $\alpha$ nuclei were located at grain corners, which they ascribed to the larger undercooling in their case compared to the study by Huang and Hillert [2]. Furthermore, Zhang et al. [5] found that almost all of the $\alpha$ nuclei had a special OR with at least one of the $\gamma$ grains at which they nucleated. As reported earlier by King and Bell [11] as well for a different alloy, most of the $\alpha$ nuclei in the study of Zhang et al. [5] had either a Kurdjumov–Sachs (K–S) or, to a lesser extent, a Nishiyama–Wassermann (N–W) ORs. Similarly, Lange et al. [11] reported that most of the $\alpha$ nuclei appeared at grain boundaries, and any nucleation occurring at grain corners was only an exception.

One of the reasons for the lack of studies of the $\alpha \rightarrow \gamma$ phase transformation is the absence of a suitable technique, which allows for in–situ observation of nucleation and growth of $\gamma$ in the bulk of the material. Recently, Savran et al. [9], have demonstrated the possibility of using synchrotron radiation to study the $\alpha \rightarrow \gamma$ phase transformation in–situ. They determined that the value of the $\Psi$ parameter is $(1.1-4.8) \times 10^{-8}$ J$^3$m$^{-6}$, similar to the case of $\gamma \rightarrow \alpha$ phase transformation reported
by Offerman et al. [12]. However, in their case, it was not possible to determine the role ORs play in the nucleation process, nor was it possible to detect all the grains in the specimen.

In the present chapter, results dealing with the role of ORs in the nucleation of the $\gamma$ phase during the $\alpha \rightarrow \gamma$ phase transformation are presented. It will be shown that observations at the level of individual grains and their neighbours are essential to understand the underlying mechanisms governing nucleation. The unique experiments and results detailed here shed new light on the evolution of the microstructure during heating and have applicability also to the $\gamma \rightarrow \alpha$ phase transformation during cooling.

6.2 Experimental methods

6.2.1 Material

The material under investigation was cast using vacuum induction casting in order to get a high-purity alloy with homogeneous composition of 0.011 wt% C, 0.87 wt% Mn, 0.083 wt% Ti and the rest Fe. The casting process was carefully monitored in order to keep the concentration of impurities very low ($<200$ ppm for all other elements combined). The specimen was manufactured using electro-discharge machining (EDM) with the dimensions shown in Figure 6.1 in order to perfectly fit in the furnace described in Chapter 2 and Reference [13]. The specimen had a change in diameter from 1 mm to 1.5 mm in the middle, which was used to define a reference by scanning with the X-ray beam. The composition of the alloy was determined using EPMA, XRF and wet chemical analysis and no chemical heterogeneities were detected.

6.2.2 3DXRD Experiment

The 3DXRD experiment was carried out at beamline ID11 of the European Synchrotron Radiation Facility (ESRF), Grenoble, France. Figure 6.2 shows the experimental setup. The specimen was placed in the 3DXRD furnace described in Chapter 2. An S-type thermocouple was spot-welded to the top of the specimen for accurate temperature control. The specimen chamber was purged with helium and sealed at a pressure of 0.4 atm. The X-ray beam, 500 $\mu$m high and 500 $\mu$m wide with energy equal to 88.005 keV, calibrated using a Pb-foil, was incident on the specimen at the location depicted in Figure 6.1. Since nucleation and growth at the surface might
slow heating to 1000 °C, homogenization at 1000 °C for 45 min in order to get coarse γ grain structure and cooling to room temperature. During the pre–heat treatment, the approximate \( \alpha \rightarrow \gamma \) transformation range was found to lie between 830 °C and 852 °C. During the experiment, so–called ‘Friedel 3D measurements’ were carried out consisting of rotating the 3DXRD furnace over a total angle of 170°, \( \omega \in [-132.5°; -47.5°] \cup [47.5°; 132.5°] \). From each Friedel 3D measurement, the volume, the centre–of–mass position and the orientation of all the grains in the illuminated volume can be determined. Diffraction images were recorded using the medium–resolution FReLoN–4M detector [14] during every 0.3° rotation with an exposure time of 0.2 s. The setup at ID11 dictates that each of the Friedel 3D measurement required a total of approx. 13 min to complete. The specimen to
Figure 6.2: Schematic showing the experimental setup. The dimensions are not to scale. The angles $2\theta$, $\omega$, and $\eta$ are defined.
essentially be different from in the bulk, the beam size chosen was smaller than the diameter of the specimen. The pre—heat treatment of the specimen involved detector distance was chosen such that four complete diffraction rings of the γ phase and three complete diffraction rings of the α phase were observed in the diffraction images. For the chosen ω—range, 29–37 or 36–45 diffraction spots should be observed from each individual α or γ grain, respectively, depending on the orientation of the grain. After an initial Friedel 3D measurement at room temperature (RT), the specimen was heated as follows:

The specimen was first heated rapidly to a temperature just below the transformation start temperature in 5 min, followed by isothermal holding for 23 min. After 10 min isothermal holding to wait for the microstructure to stabilize, a Friedel 3D measurement was carried out, at the end of which, the temperature of the specimen was increased by 2 °C in 2 s. At the raised temperature, another Friedel 3D measurement was carried out after 10 min in order to capture the microstructure of the specimen after stabilization. This heating by 2 °C, wait for 10 min followed by a Friedel 3D measurement was repeated until a temperature of 852 °C was reached. The specimen was then heated to a temperature of 900 °C in 60 s and held isothermally for 130 min followed by cooling to room temperature. The heat treatment is also shown schematically in Figure 6.3.

In total, 23 Friedel 3D measurements were carried out, i.e., information about the (partial)—3D microstructure of the specimen was obtained at 23 points during the heat treatment.

6.3 Data analysis method

6.3.1 Pre—processing

The procedure mentioned in Chapter 3 was followed in order to characterize the diffraction spots from the raw diffraction images. A low threshold of 150 counts was used in order to identify regions consisting of diffracted intensity. After peak searching and fitting, almost 99% of the diffraction spots were correctly identified. The global parameters of the experiment were determined from the diffraction data itself and no calibration specimen was required, as described in Chapter 3.
6.3. Data analysis method

6.3.2 Fraction transformed

In order to calculate the fraction transformed at each point during the phase transformation, all the diffraction images recorded during a Friedel 3D measurement were summed in order to get powder–like diffraction images. After a radial integration step on the summed image, the fraction transformed was calculated according to the procedure described in Reference [15].

6.3.3 Indexing and refinement

In order to keep the processing time low, indexing and refinement routines were executed on each Friedel 3D measurement with the following parameters:

Figure 6.3: Schematic of the heat treatment carried out on the specimen. During the step–wise heating from 830 °C to 852 °C in 2 °C steps, after a stabilization step for 10 min, a Friedel 3D measurement is carried out at each step. At the isothermal annealing temperature of 900 °C, Friedel 3D measurements were carried out a total of 10 times.
6. The role of orientation relationships during nucleation of austenite

Diffraction spots belonging to the \{200\} planes were chosen as staring points for indexing. Since the \{110\} ring of \(\alpha\) and \{111\} ring of \(\gamma\) overlap, all the diffraction spots belonging to these two rings were omitted from analysis during the phase transformation. A 5 \(\mu\text{m}\) step in the position in the specimen and 0.2° step in the rotation of the diffracting plane normal were used during indexing (see Chapter 4 for details). The margins that were used around the theoretical position of the diffraction spots on the detector are 60 \(\mu\text{m}\) and 0.4°, respectively in position on the detector and in \(\omega\). Detection of both the symmetric and the asymmetric Friedel pairs was switched on. All the grains for which the mean difference in \(\omega\) was less than 0.06° and the mean difference in the position of the observed and the simulated diffraction spots on the detector was less than 25 \(\mu\text{m}\) were identified and stored as grains that are correctly indexed. See Chapter 4 for details about the settings.

Due to the horizontal size of the X-ray beam being smaller than the diameter of the specimen during rotation, the volume of the specimen that was illuminated by the X-ray beam changed continuously, though a smaller cylinder of diameter equal to the width of the beam was always in the beam. This is shown schematically in Figure 6.4. Due to this, firstly, the volume of a grain located at the edge of the smaller cylinder that gives rise to diffraction was different each time. Secondly, for the grains located outside this cylinder, not all diffraction spots are observed because the grains are not always in the beam. Therefore, three filtering steps were used: (\(i\)) the minimum fraction of observed diffraction spots related to one specific grain divided by the simulated diffraction spots was chosen to be 0.8; (\(ii\)) the difference between the grain size as calculated from a starting diffraction spot and the grain sizes as calculated from the other diffraction spots being matched during indexing to the same grain was chosen to be less than 10 \(\mu\text{m}\) in grain radius and; (\(iii\)) a grain was accepted only if the refined centre-of-mass position of the grain was within the smaller cylinder (henceforth called the ‘cylinder’) defined by the beam size. In the case of the grains close to the edges of the cylinder, the uncertainty in the centre-of-mass position, the orientation and the volume of the grains is higher than for that for the grains located completely in the cylinder.

At each point during the phase transformation, since the Friedel 3D measurements were carried out only after the equilibrium fraction transformed had been reached at that particular temperature, not all the grains were observed at the nucleation stage. In the results shown here, the minimum radius of the \(\gamma\)-grains when first detected (calculated from volume assuming spherical shape) is between 4.8 to 12 \(\mu\text{m}\), since all \(\gamma\) nuclei had already grown before the start of the Friedel 3D
Figure 6.4: Schematic top view of the illuminated volume of the specimen during different orientations of the X-ray beam (the synchrotron is assumed to rotate, instead of the specimen). The smaller cylinder that is investigated in the present study is shown. The cylinder has a diameter equal to 500 µm.

measurements. Compared to the coarse starting α microstructure (average grain size of ~105 µm) and the ending γ microstructure (average grain size of ~98 µm), this is not expected to have a significant effect during detection of neighbours of the γ nuclei. However, the volume of the smallest grains, which could be detected at
any time during the experiment (determined by the threshold used) was $\sim 120 \, \mu\text{m}^3$ ($\sim 3 \, \mu\text{m}$ radius), so that all the grains above this size could successfully be identified. Thus, even though grains with a radius of $3 \, \mu\text{m}$ in radius could be identified, no $\gamma$ nuclei of such small size were found because the $\gamma$ nuclei had already grown to large sizes before the Friedel 3D measurements were carried out.

### 6.3.4 $\gamma - \alpha$ neighbour detection

In the experimental setup, diffraction images were recorded using only the medium-resolution FReLoN–4M detector, due to which the geometry of the grain boundaries could not be determined. The shape of the grains were approximated by ellipsoids with small aspect ratios. The strategy to determine, in which $\alpha$ grains, a $\gamma$ grain has grown soon after nucleation is as follows:

The distance between the center-of-mass of a $\gamma$ grain (at the time when it was first detected and thus relatively small) and that of each $\alpha$–grain in the illuminated volume was calculated first including a factor to account for the uncertainty in the position of the grains. This distance was normalized by the radius of the corresponding $\alpha$ grain to calculate a so-called ‘sphere of influence’ of the $\alpha$ grain. The $\alpha$ grains for which this sphere of influence had a value smaller than 1.5 were identified as possible neighbours of the $\gamma$ grain under consideration henceforth referred to as the candidate $\alpha$ grains. This step makes sure that if the $\alpha$ grain is identified as a neighbour in the end, the shape of the grain is still close to an ellipsoid with a maximum aspect ratio of 1.5. Repeated calculations showed that the choice of the maximum aspect ratio had no significant influence up to a value of 2.

For each of the candidate $\alpha$ grains, the 3D space was divided into half. This was done by transforming the coordinates of all the $\alpha$ grains in such a way that the $z$–axis of position coordinates was aligned in the direction from the center-of-mass of the $\gamma$ grain towards the candidate $\alpha$ grain. In case the sphere of influence of the $\alpha$ grain in question was less than the sphere of influence of the remaining $\alpha$ grains (with positive value of transformed $z$–position) that are closer to the $\gamma$ grain (in absolute distance) as compared to the $\alpha$ grain in consideration, the $\alpha$ grain was identified as a neighbour of the $\gamma$ grain. In case there were $\alpha$ grains with the sphere of influence smaller than the original $\alpha$ grain, the absolute distance between the $\alpha$ grains and the $\gamma$ grain was compared and the $\alpha$ grain positioned at the smallest absolute distance from the $\gamma$ grain was saved as a neighbour of the $\gamma$ grain.
6.3.5 Orientation Relationships

In order to define a special OR between the \( \gamma \) and the \( \alpha \) neighbours detected in the previous step, the following procedure was followed:

First, the angles between the \( \{110\}_\alpha \) planes and the \( \{111\}_\gamma \) planes were calculated. If the minimum of these angles was below 3°, the deviation angles between the \( <111>_\alpha \) directions and the \( <110>_\gamma \) directions were calculated. The deviation angles between the directions were defined as the projection of the \( <111>_\alpha \) directions and the \( <110>_\gamma \) directions in the matched \( (111)_\gamma \) plane. A special OR was detected if the minimum of the deviation angles was below 12°. The directions used for matching correspond to the K–S OR and, since the N–W OR is only 5.26° off from the K–S OR, it was detected automatically as well. The sign of the deviation angle was chosen according to the following rule:

\[
\text{Deviation} \angle_{K-S} = \begin{cases} 
\text{negative} & \text{if Deviation} \angle_{K-S} < 5.26 < \text{Deviation} \angle_{N-W} \\
\text{positive} & \text{otherwise}
\end{cases} \tag{6.3}
\]

6.4 Results and discussion

The \( \gamma \) fraction as a function of temperature is shown in Figure 6.5. It can be seen that the transformation starts very rapidly, with almost 20% of \( \alpha \) transforming to \( \gamma \) in the first step of 2 °C. The \( A_1 \) and \( A_3 \) temperatures calculated using Thermo–Calc\textsuperscript{®} under ortho–equilibrium conditions are 845 °C and 878 °C, respectively, which differ significantly from the experimental \( A_1 \) and \( A_3 \) temperatures of around 832 °C and 848 °C.\footnote{There is a maximum inaccuracy of 2 °C, equal to the step size during heating, in the values determined from the 3DXRD experiment.} However, the \( A_1 \) and \( A_3 \) temperatures determined from dilatometer experiments using a heating rate of 2 °C/min were 833 °C and 852 °C, respectively, which are quite close to the values measured from the 3DXRD experiment.

Figure 6.6 shows the evolution of the number of grains in the cylinder (Figure 6.4) in the specimen as a function of temperature. It can be seen that the total number of grains, \( i.e., \) the sum of the \( \alpha \) and the \( \gamma \) grains in the cylinder (blue colour), does not change too much during the transformation. A remarkable feature of Figure 6.6 is the difference between the accumulated number of \( \gamma \) grains and the number of \( \gamma \) grains in the cylinder at the corresponding temperatures. This difference represents the number of \( \gamma \) grains, which, although present in the
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Figure 6.5: $\gamma$ fraction as a function of temperature.

microstructure at temperature, $T_{n-1}$, have disappeared at temperature, $T_n$. This is very interesting, since a number of $\gamma$ grains, totalling 48, disappeared during the phase transformation. One of these grains was almost 120 $\mu$m in diameter before it was consumed by other $\gamma$ grains.

The microstructure before the phase transformation at 830 $^\circ$C (fully $\alpha$) and after the completion of the phase transformation at 848 $^\circ$C (fully $\gamma$) and the evolution of the microstructure during the phase transformation is shown in Figure 6.7. The plots in rows 1 and 3 show the centre−of−mass position of the $\alpha$ grains and the plots in rows 2 and 4 show the centre−of−mass position of the $\gamma$ grains at different stages of the phase transformation. Each marker in Figure 6.7 represents a grain, the colour of the marker corresponds to the orientation of the grain and the size of the marker is equal to the radius of the grain divided by 2.5. This factor is chosen for
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Figure 6.6: Number of grains in the cylinder as a function of temperature. The number of γ grains (black) is the number of γ grains present in the cylinder at a certain temperature while the total number of γ grains (green) is the total number of γ grains, which were detected until that corresponding temperature.

representation purposes. Small displacements (up to 15 µm) in the position of the grains were observed at different stages. These displacements might correspond to changes in the centre−of−mass position of the grains or to the uncertainty in the position of the centre−of−mass of the grains.

The γ grain information can be used to calculate the number of new γ nuclei as a function of temperature, shown in Figure 6.8. Also shown is the normalized number of γ nuclei per unit untransformed volume. If only the number of γ nuclei is considered, the trend shows a definite peak. However, correction for the number of potential nucleation sites by calculating the normalized number of γ nuclei per unit untransformed volume shows clearly a rapid increase as the temperature
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Figure 6.7: Evolution of the microstructure of the specimen during the $\alpha \rightarrow \gamma$ phase transformation. (a, b, c, f, g) Position of the $\alpha$ grains. (d, e, h, i, j) Position of the $\gamma$ grains. The axis units are $\mu$m. The size of each marker is equal to the size of the corresponding grain divided by 2.5. The division by 2.5 is needed to visualise the microstructure. The two blue circles in each plot indicate the size of the cylinder (500 $\mu$m diameter). Colours represent orientation according to the colour legend (Euler angles). (a) Microstructure before the phase transformation at 830°C. (b, d) Microstructure at 836°C. (c, e) Microstructure at 840°C. (f, h) Microstructure at 844°C. (g, i) Microstructure at 846°C. (j) Microstructure after the phase transformation at 848°C.
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Figure 6.8: Nucleation characteristics during the phase transformation. Black bars show the number of new γ nuclei appearing per temperature interval (nucleation rate). The red bars show the normalized nucleation rate per unit untransformed volume. The magenta and black curves show the fit to Equation 6.2 using the two different \( \Delta g_v \) values: using no partitioning of Mn and Ti (magenta) and using the parallel tangent construction for the maximum driving force (black). All C (and proportionately Ti) was removed from calculations by fixing as TiC precipitates.

Increases. This is in agreement with the exponential terms in Equation 6.2 which predicts a rapid increase in the nucleation rate with increasing temperature. Figure 6.8 also clearly shows that nucleation of new γ grains occurs throughout the phase transformation and does not stop after the formation of γ nuclei only at the beginning of the transformation.

In order to calculate the \( \Psi \)—parameter, the driving force for nucleation, \( \Delta g_v \), was calculated from Thermo-Calc\textsuperscript{13}. As described previously, the \( A_1 \) and \( A_3 \) temperatures calculated from Thermo-Calc\textsuperscript{13} did not match the \( A_1 \) and \( A_3 \) temperatures calculated from the 3DXRD experiment. In order to overcome this mismatch, the \( \Delta g_v \) values were converted from the absolute temperatures to overheating, \( \Delta T \), values.
Here the assumption is that the slope of $\Delta g_v$ as a function of $\Delta T$ should be correct, even though the $A_1$ and $A_3$ temperatures do not match. Aaronson and co–workers have already shown this to be the case for ortho– and para–equilibrium conditions \[16,17,18\]. Furthermore, since the effective heating rate is 0.087 $^\circ$C/min, equilibrium conditions were assumed. The formation of TiC precipitates was assumed to be complete during the whole duration of the heat treatment because the specimen was cooled slowly during the pre–heat treatment and heated slowly during the experiment. Due to the higher atomic fraction of Ti in the alloy as compared to C, all the C was assumed to have been consumed by the TiC precipitates and only a lower amount of Ti (0.0455 at%) and the full amount of Mn was used during the $\Delta g_v$ calculation. $\Delta g_v$ was then calculated in two ways:

(i) Fixing the composition of both the matrix ($\alpha$) and the forming ($\gamma$) phases to be equal, assuming that Mn and Ti do not have enough time to partition during the transformation. The value of the $\Psi$–parameter calculated from the best fit of Equation 6.2 to the nucleation rate, shown in Figure 6.8, is $2.96 \times 10^{-8} J^3 m^{-6}$.

(ii) Allowing for partitioning of Mn and Ti and calculating $\Delta g_v$ using the parallel tangent construction \[17\]. The value of the $\Psi$–parameter calculated from the best fit of Equation 6.2 to the nucleation rate, Figure 6.8, is $4.64 \times 10^{-8} J^3 m^{-6}$.

The calculated $\Psi$ values are similar to the value calculated by Offerman et al. \[4,12\] for the $\gamma \rightarrow \alpha$ phase transformation ($5 \times 10^{-8} J^3 m^{-6}$) and the values calculated by Savran et al. \[9\] for the $\alpha \rightarrow \gamma$ phase transformation (between $4.8 \times 10^{-8} J^3 m^{-6}$ and $1.1 \times 10^{-8} J^3 m^{-6}$). The results of the fits using the two types of $\Delta g_v$ values are shown in Figure 6.8. The two curves are almost indistinguishable. During fitting, $Q_D$ was included as an unknown parameter and was fitted as well. The fitted value of $Q_D$ was found to be $3.75 \times 10^{-19} J$ and $3.72 \times 10^{-19} J$ for the no partitioning and parallel tangent construction cases, respectively. These values are close to, although a bit lower than, the value of $3.93 \times 10^{-19} J$ reported in literature for self–diffusion of Fe atoms in paramagnetic $\alpha$ \[19\].

Using the criteria mentioned in §6.3.5, ORs between each $\gamma$ grain and the neighbouring $\alpha$ grains were calculated. The distributions of these deviations for are shown in Figure 6.9. Also highlighted is the position of the ideal K–S and the ideal N–W OR. It must be noted here that the average error in the crystallographic orientation of an $\alpha$ grain is around 0.04°. The mosaicity of the $\alpha$ grains, which limits the maximum amount by which the orientation at grain boundaries can be different from the average orientation of the grains, which is measured here, was between 0.13° to 1.2°. The uncertainty in the average orientation, combined with
the uncertainty in the orientation at the grain boundaries (around half the value of the mosaicity), still defines that, for deviation angles greater than 0.1° to 0.65° (depending on the grain), the possibility of the existence of a perfect special OR can be ruled out for most of the γ−α pairs. A unique feature of Figure 6.9 is that no γ−α pairs close to the ideal N−W OR have deviation angles from the parallel plane condition lower than 0.25°, whereas this is the case for a significant number of γ−α pairs close to the ideal K−S OR.

Figure 6.10 shows a polar plot of the histogram of the deviation angle from the parallel direction condition for the K−S OR. Also shown is the angle for the ideal direction for the N−W OR. It can be seen from Figure 6.10 that a large number of
Figure 6.10: Polar plot of the histogram of the deviation angles from the parallel direction condition for the K–S OR for all the $\gamma - \alpha$ pairs shown in Figure 6.9. The horizontal axis (0°) represents the ideal K–S OR ($<111>_{\alpha} \parallel <110>_{\gamma}$). The ideal N–W OR ($<100>_{\alpha} \parallel <110>_{\gamma}$) is at an angle of 5.26° from the ideal K–S OR.
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\(\alpha - \gamma\) pairs have deviation angles away from N–W (negative angles in Figure 6.10). For these \(\alpha - \gamma\) pairs, even though the deviation from the parallel direction condition of K–S OR is lower than 4\(^\circ\), the deviation from the parallel direction condition of N–W OR is greater than 5.3\(^\circ\) and can thus be associated with the K–S OR than with the N–W OR. Furthermore, only N–W OR (pairs closer to the ideal N–W condition than to the ideal K–S condition) was not observed for any of the \(\gamma\) nuclei. In case a \(\gamma\) nucleus had N–W OR with a neighbouring \(\alpha\) grain, it was observed that this \(\gamma\) nucleus always had a K–S OR with at least one other \(\alpha\) grain.

It can be inferred from Figure 6.9 and Figure 6.10 that the number of N–W \(\gamma - \alpha\) pairs (points closer to ideal N–W than to K–S) is lower than K–S \(\gamma - \alpha\) pairs and almost 74% of the ORs are of the K–S type. This result is consistent with the observations of Zhang et al. [5], where K–S OR was found to be more dominant than N–W and the calculations of Nagano and Enomoto [20], who showed that the activation energy for nucleation should be smaller for K–S than that for N–W based on the smaller calculated size of the nucleus in Wulff space for K–S than that for N–W.

Figure 6.11 shows a polar plot of the histogram of the deviation from the parallel plane condition for the \(\gamma - \alpha\) pairs shown in Figure 6.9. As far as atomic matching across the \(\gamma - \alpha\) interface is concerned, it appears that it is more difficult for the two planes to be away from the parallel condition than for the directions, which can be seen from both Figure 6.9 and Figure 6.11. For a majority of the \(\gamma - \alpha\) pairs for which the deviation from the parallel direction condition is up to 5\(^\circ\), the deviation from the parallel plane condition is only up to 3\(^\circ\).

As described in §6.1, the activation energy for nucleation, \(\Delta G^*\), is strongly affected by the \(\Psi\)–parameter, which, in turn, depends on (i) the shape of the \(\gamma\) nucleus; (ii) the energy of the \(\alpha - \alpha\) interfaces, which are replaced during nucleation and; (iii) the energy of the \(\gamma - \alpha\) interfaces, which are formed during nucleation. In terms of the interface energies, the best situation for a theoretically high nucleation rate (the lowest \(\Psi\) value) would be when the total energy of the \(\alpha - \alpha\) interfaces being replaced is high and the energy of the \(\gamma - \alpha\) interfaces being formed is low. Thus, in simple terms, the \(\alpha - \alpha\) grain boundaries (or corners or edges) that should be the optimum sites for nucleation of \(\gamma\) grains are the \(\alpha - \alpha\) grain boundaries for which it is possible to have special ORs (read: low energy \(\gamma - \alpha\) interfaces) with the \(\gamma\) grains.

To test the hypothesis described above, the number of \(\alpha\) neighbours having a special OR with a \(\gamma\) nucleus was calculated. This is shown in Figure 6.12. It can
be seen that more than a third of the total \( \gamma \) nuclei have a special OR with only one \( \alpha \) grain, whereas more than half of the \( \gamma \) nuclei have a special OR with two or more \( \alpha \) grains. Around 93% of the \( \gamma \) nuclei have a special OR with at least one \( \alpha \) grain. This is consistent with the results of Zhang et al. [5]. No \( \gamma \) nuclei having special ORs with five or more \( \alpha \) neighbours were detected. Since the geometry of the grain boundaries were not detected in the present experiment, the technique has a disadvantage: even with the sophisticated criterion used to detect neighbours, some grains might be detected which were not neighbours in reality. This has a direct influence that, in the case of a few \( \gamma \) grains, which were found to have an OR
with four \( \alpha \) neighbours, in reality a lesser number of \( \alpha \) grains (two or three) had an OR. This would, to a much lesser extent, also affect the number of \( \gamma \) grains having an OR with three neighbouring \( \alpha \) grains.

Figure 6.12 shows that the number of \( \gamma \) nuclei having a special OR with either three or four \( \alpha \) grains is lower than those having a special OR with either one or two \( \alpha \) grains. However, according to the aforementioned hypothesis, the number of \( \gamma \) nuclei having a special OR with four \( \alpha \) grains should be the highest, due to the maximum nucleation rate associated with the low energy \( \gamma - \alpha \) grain boundaries that are formed. Thus, the number of \( \gamma \) nuclei should increase with the number of \( \alpha \) neighbours with which a special OR exists. The results of Figure 6.12 can be understood by examining Equation 6.1. In addition to the \( \Psi \)-parameter, which should decrease as the number of \( \alpha \) neighbours with which a \( \gamma \) grain has a special OR increases, the nucleation rate in Equation 6.1 is also dependent on the density of potential nucleation sites, \( N_v \). \( N_v \) depends on the type of nucleation site, e.g., it is highest for homogeneous nucleation inside grains and lowest for grain corners [21]. In the case of nucleation of a \( \gamma \) grain with a special OR with two or more \( \alpha \) neighbours, special ORs between the \( \alpha \) neighbours are required as well. As a consequence, the density of the nucleation sites for which the \( \gamma \) nucleus would have a special OR with three or four \( \alpha \) grains (\( \gamma_{3-4} \)) can be expected to be lower than those for which the \( \gamma \) nucleus would have a special OR with only one or two \( \alpha \) grains (\( \gamma_{1-2} \)), which means a lower nucleation rate for \( \gamma_{3-4} \) type of nuclei than for \( \gamma_{1-2} \) type. Furthermore, the only potential nucleation sites for \( \gamma \) nuclei having special ORs with four \( \alpha \) neighbours are grain corners, while nucleation of \( \gamma \) nuclei having special ORs with three, two and one \( \alpha \) neighbours is possible at edges, faces and (corners, edges and faces), respectively. Since the number of grain corners is lower than edges, for instance, the density of potential nucleation sites is consequently lower for \( \gamma \) nuclei having special ORs with four \( \alpha \) neighbours than the other types of \( \gamma \) nuclei.

If the requirement of the existence of special ORs between the \( \alpha \) grains in order for a \( \gamma \) grain to nucleate at the boundary (or edge or corner) is considered, then the results in Figure 6.12 hint at the presence of a special starting \( \alpha \) microstructure, where almost a third of the nucleation\(^2\) occurred at special \( \alpha - \alpha \) grain corners (or edges or boundaries). As described in §6.2, the specimen was manufactured from a cast alloy and was austenitized prior to the heat treatment in order to get big \( \alpha \)

\(^2\)For \( \gamma \) nuclei having a special OR with three or four \( \alpha \) neighbours.
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Figure 6.12: Histogram of the number of $\alpha$ neighbours having an OR with a $\gamma$ nucleus.

grains. Thus, it is very interesting to find out why such a special microstructure would exist in the specimen.

In order to understand the formation of this special microstructure, consider the formation of $\alpha$ from $\gamma$ during cooling. Since the specimen was cooled at a relatively fast rate, and since the observed number of $\gamma$ nuclei during heating with a very low (effective) rate is already high compared to the number of $\alpha$ grains, the nucleation rate of $\alpha$ in $\gamma$ during cooling might have been very high. In that case, if multiple $\alpha$ grains nucleate on the boundaries of a $\gamma$ grain, each $\alpha$ grain having a special OR with the starting $\gamma$ grain but as a different variant, the $\alpha$ grains have a special OR with each other. Later, during heating, a $\gamma$ grain, with the same orientation as the parent $\gamma$ grain on which the $\alpha$ grains had nucleated, can nucleate at the corner formed by the $\alpha$ grains and will have an OR with all the $\alpha$ grains. This would especially be true during cooling, since grain coarsening occurs to a much smaller...
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Figure 6.13: Schematic of the mechanism, which can result in a high density of special nucleation sites allowing for $\gamma$ nuclei to have ORs with multiple $\alpha$ grains. Thick red lines show the grain boundaries with a special OR.

extent due to the lower temperatures involved, so that most of the $\alpha$ grains survive. This process is shown schematically in 2D in Figure 6.13 where multiple $\alpha$ grains nucleate on a $\gamma$ grain ($\gamma_0$) during cooling. During heating, another $\gamma$ grain ($\gamma_f$) nucleates at the triple point of the three $\alpha$ grains ($\alpha_1$, $\alpha_3$, $\alpha_4$). $\gamma_f$ has the same orientation as $\gamma_0$. In 3D, this scenario is replaced by nucleation at grain corners.

This phenomenon, during a heating–annealing–cooling cycle would also result in the texture memory effect [22]. However, during the annealing step, if enough coarsening of $\gamma$ grains takes place, the texture memory effect would disappear. It must be noted here that this mechanism requires nucleation densities of more
than one $\gamma$ nucleus per $\alpha$ grain during the $\alpha \rightarrow \gamma$ phase transformation and a lower nucleation density during the $\gamma \rightarrow \alpha$ phase transformation.

An interesting feature of the mechanism presented is as follows: in the texture memory effect, the retention of texture is commonly associated with much faster heating and cooling rates than the ones studied here [22]. However, according to the present observations, a high nucleation rate is the only requirement, which might as well be controlled either by alloying or by changing the heating and/or cooling rates. Furthermore, even for macroscopically randomly textured materials, this effect would create very special microstructures, the detection of which would be impossible without examining the micro-structure of the different neighbours. The microstructure, both before and after the phase transformations, would still retain a random texture, but with special qualities of neighbouring grains.

For the 38 $\gamma$ grains, which nucleated with a special OR with four neighbouring $\alpha$ grains, of the 152 possible $\alpha$ neighbours with a special OR, 99 were unique. This means that 99 $\alpha$ grains were responsible for the nucleation of 38 $\gamma$ grains having a special OR with four neighbouring $\alpha$ grains. Out of these 99 grains, 29 had small misorientations ($<5^\circ$) with respect to each other and formed 37 possible Low Angle Grain Boundaries (LAGBs). Thus, out of the total 152 $\alpha-\alpha$ grain boundaries, which were (possibly) replaced during $\gamma$ nucleation, only 37 (24%) were LAGBs (read: low energy).³ This is consistent with the hypothesis that the maximum nucleation rate should be for the cases where high-energy interfaces are replaced by low energy interfaces (with an OR). However, it was found that nucleation at only LAGBs was not observed and in each case at least one HAGB was involved. The fraction of LAGBs involved during nucleation is similar to the observations of Zhang et al. [5] for the $\gamma \rightarrow \alpha$ phase transformation, who observed that 25% of $\gamma$ nuclei at the grain corners involved at least one $\gamma-\gamma$ LAGB.

Due to the strong dependence of the $\Psi$—parameter on the $\gamma-\alpha$ interface energies, it should be expected that the different $\gamma$ nuclei with different number of $\alpha$ grains with a special OR would nucleate at different times (or at different temperatures) during the phase transformation. The nucleation temperature as a function of the number of $\alpha$ neighbours with a special OR for the $\gamma$ grains in the cylinder is shown in Figure 6.14. A remarkable feature of Figure 6.14 is that, consistent with the aforementioned hypothesis, the maximum in the number of $\gamma$ nuclei having a special OR with four $\alpha$ grains is observed at the lowest temperature. As the

³Here only LAGBs were considered and other low energy grain boundaries, such as $\Sigma$—type of grain boundaries, were not considered.
Figure 6.14: Nucleation temperature as a function of the number of $\alpha$ neighbours with an OR. The total number of $\gamma$ nuclei (black) is the sum of each type (0, 1, 2, 3 and 4) and the same as in Figure 6.8.
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number of $\alpha$ neighbours with a special OR decreases, the temperature, at which the maximum number of $\gamma$ nuclei is observed, increases. The $\gamma$ nuclei having a special OR with none of the $\alpha$ neighbours, with the exception of two $\gamma$ nuclei, peak towards the end of the transformation (at the highest temperatures), which means highest $\Delta T$. The decrease in the number of $\gamma$ nuclei of any type as the temperature increases might be due to site saturation.

Figure 6.14 shows that the nucleation temperature of various types of $\gamma$ grains depends on the number of neighbours with a special OR. This means that a single value of the $\Psi$–parameter should be used with due caution for calculating the nucleation rate. Using the individual curves shown in Figure 6.14 (b), the $\Psi$ values for each type of $\gamma$ nuclei having a special OR with one, two, three and four neighbouring $\alpha$ grains was calculated. The $\Delta g_v$ value corresponding to the parallel tangent construction was used during fitting. In order to calculate the density of nucleation sites for each type of $\gamma$ nuclei, it was assumed that the number of potential nucleation sites at a temperature interval, $T_n$, is directly proportional to the total number of $\gamma$ nuclei present at $T_n$ added with all the $\gamma$ nuclei, which appear at higher temperatures.

Even though Zhang et al. [23] have shown for the $\gamma \rightarrow \alpha$ phase transformation that nucleation did not occur at all the grain corners in a Co–15Fe alloy, if the evolution of the nucleation rate is similar to the evolution of the number of nucleation sites, the value of $\Psi$ is not affected and only the absolute number of nucleation sites might differ. The number of potential nucleation sites at a temperature interval $T_n$ was calculated as:

$$N_n \propto \sum_{i=n}^{\text{end}} A_i$$  \hspace{1cm} (6.4)

where, $A_i$ is the number of $\gamma$ nuclei appearing at temperature interval $T = T_i$. The results of best fit to $\dot{N}_j$ in Equation 6.1 for each type of nuclei are shown in Figure 6.15. It is evident that the temperature, at which the maximum in the nucleation rate is observed, is reproduced very well in the fitted curves. This is important to judge the quality of the results because, for fixed $N_v$ and $\Delta g_v$, only

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[4] It is not possible to do the same for $\gamma$ nuclei having a special OR with none of the $\alpha$ neighbours due to the low number of data points available for fitting.

[5] This assumption means that the evolution of the number of nucleation sites is assumed to be the same as the evolution of the nucleation rate. This assumption would underestimate $\Psi$ in case the nucleation sites are consumed by growing $\gamma$ grains during the phase transformation.
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(a) (c)

(b)

1 OR

Fit

2 ORs

Fit

Nucleation rate

Temperature (°C)

0 5 10 15 20 25 30 35

0 10 20 30

830 832 834 836 838 840 842 844 846 848 850

180
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Figure 6.15: Results of fitting nucleation rate as a function of temperature for the case of \( \gamma \) nuclei having a special OR with (a) one; (b) two; (c) three and; (d) four neighbouring \( \alpha \) grains. The red bars show the nucleation rate, calculated according to the number of \( \gamma \) nuclei of a certain type appearing at a given temperature interval. The black curves represent the fitted nucleation rate according to Equation 6.1.
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Type of γ nuclei  | Ψ (J^3m^{-6} [×10^{-8}]  | Q_D (J) [×10^{-19}] |
--- | --- | --- |
Total | 4.64 | 3.72 |
1 OR | 7.03 | 3.73 |
2 ORs | 6.59 | 3.76 |
3 ORs | 5.85 | 3.76 |
4 ORs | 1.59 | 3.80 |

Table 6.1: Ψ and Q_D values obtained after fitting for different types of γ nuclei.

The values of Ψ and Q_D obtained from the best fits for each type of γ nuclei are shown in Table 6.1. It can be seen that Ψ for the γ nuclei having special ORs with four α neighbours is lower than the other types and it increases as the number of α neighbours with a special OR decreases. This is consistent with the definition of Ψ, which dictates that Ψ increase as the total contribution of the low energy interfaces (read: interfaces with special ORs) decreases. The lowest value of Ψ means that, out of the four types of γ nuclei (having one, two, three and four special ORs), nucleation rate is highest for the γ nuclei having special ORs with four α neighbours. It is interesting to note that, except for the γ nuclei having special ORs with four α neighbours, the difference between the calculated value of Ψ for the γ nuclei having special ORs with one, two or three α neighbours is around 6–11%. Furthermore, it can be seen that the fitted values of the activation energy for atomic migration across the γ–α interface, Q_D, for the different types of γ nuclei is similar to the value obtained for the total number of γ nuclei and the value of Q_D for self–diffusion of Fe in paramagnetic α reported in literature [19].

In the present analysis, only one of the factors influencing Ψ is considered: the (possible) low energy of the γ–α interfaces by considering ORs, which are created during nucleation, but the energy of the (possibly) other γ–α interfaces without ORs is not considered. The other two factors, which influence Ψ namely, the energy of the α–α interfaces, which are replaced during nucleation and, the shape of the critical γ nuclei are not investigated in the present analysis. Furthermore, the nature of the nucleation sites, i.e., corner, edge, face or intra-granular, cannot be determined from the present measurements. This is mainly due to two reasons: (i) the geometry of the grain boundaries is not known and; (ii) the inaccuracy in

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As mentioned earlier, Q_D for self–diffusion of Fe in paramagnetic α is 3.93 × 10^{-19} J.
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the position of the centre–of–mass of the $\gamma$ nuclei is far too high (up to 15 $\mu$m) to pinpoint the exact location of nucleation. Thus, the present study investigates only one aspect of nucleation and new experiments capable of yielding information about the rest of the parameters should be designed.

6.5 Conclusions

The nucleation of $\gamma$ grains in a Fe–C–Mn–Ti alloy during step–wise heating was studied using 3DXRD microscopy. The following conclusions can be drawn:

(i) At all temperatures during the transformation, new $\gamma$ nuclei appeared. The number of $\gamma$ nuclei per unit untransformed volume increased rapidly with increasing temperature. The total number of $\gamma$ nuclei in the specimen was almost 1.4 times the total number of $\alpha$ grains before the transformation. A number of $\gamma$ grains in the specimen were consumed by other $\gamma$ grains during the phase transformation. Surprisingly, one $\gamma$ grain, as large as 120 $\mu$m in diameter, disappeared during the transformation.

(ii) The overall $\Psi$–parameter, which represents the effects of the shape of the nucleus and the interface energies between the nucleus and the matrix and between the matrix grains, was found to be similar to the values reported for the $\alpha \rightarrow \gamma$ and the $\gamma \rightarrow \alpha$ phase transformations ($2.9 - 4.6 \times 10^{-8}$ J$^3$m$^{-6}$).

(iii) The K–S OR was found to be more abundant than the N–W OR for the $\gamma$ nuclei. Furthermore, the N–W OR had small deviations from the parallel plane condition less frequently than the K–S OR, which might explain why N–W OR was observed less frequently than the K–S OR.

(iv) Most of the $\gamma$ nuclei (~93%) had a special OR (N–W or K–S) with at least one of the neighbouring $\alpha$ grains. More than half of the $\gamma$ nuclei had a special OR with two or more $\alpha$ neighbours. The surprising result is the observed high frequency of occurrence of $\gamma$ nuclei having a special OR with three and four $\alpha$ neighbours, indicating the presence of a very special microstructure. Each of the three (or four) $\alpha$ neighbours in the microstructure have a special OR with each other as well, being different variants of the same $\gamma$ nucleus. A high nucleation density of $\alpha$ grains with special ORs during cooling (multiple $\alpha$ grains per starting $\gamma$ grain) coupled with minimal coarsening of the $\alpha$ grains is proposed as a possible mechanism of the formation of this special microstructure.

(v) The $\Psi$–parameter was divided into five categories depending on the number
6. The role of orientation relationships during nucleation of austenite

of $\alpha$ neighbours with a special OR. The $\gamma$ grains having special ORs with four $\alpha$ neighbours have the lowest value of $\Psi$, followed, in order, by $\gamma$ grains having special ORs with three, two and one $\alpha$ neighbours. This means that the nucleation rate is highest for the $\gamma$ grains having special ORs with four $\alpha$ neighbours. The $\gamma$ grains nucleating without a special OR with any of the $\alpha$ neighbours appear towards the end of the phase transformation.

The observations presented here are very unique in nature and are considered immensely beneficial for a better understanding of nucleation in metals, both during heating and cooling.

6.6 Bibliography


CHAPTER 7

GRAIN COARSENING IN 
NIOBium CONTAINING STEELS 
STUDIED BY 3DXRD

Abstract

Coarsening of austenite ($\gamma$) grains in alloys containing Nb with Nb:C atomic ratios greater than unity (1.3:1 and 11.5:1) was investigated in situ using 3-Dimensional X-Ray Diffraction (3DXRD) microscopy. The alloys were annealed isothermally at three temperatures each: 1000 °C, 1050 °C and 1100 °C for the low Nb alloy and 960 °C, 1000 °C and 1100 °C for the high Nb alloy. The results of isothermal annealing revealed a very interesting behaviour: almost no significant change in the average $\gamma$ grain size in the alloys at temperatures up to 1100 °C for durations greater than 2 h. However, changes in grain volume at the level of individual grains were observed. Almost none of the grains in the specimens disappeared during the isothermal annealing. Remarkably, grains smaller in radius than $\sim$40 µm and $\sim$15 µm in the low Nb and the high Nb specimens, respectively, showed a net increase in grain volume, whereas larger grains showed a net decrease in grain volume. These results are in contrast with ‘normal’ grain coarsening behaviour of a Fe–2 wt% Mn alloy shown in Chapter 5 and with the traditional models and theories of grain coarsening. Strong segregation of Nb atoms to grain boundaries is proposed as a
possible mechanism for the observations. The alloys designed and studied here exhibit very unique combination of properties: the possibility of achieving small \( \gamma \) grain size during heating and limited or no grain coarsening (average grain size) at temperatures up to 1100 °C and possibly higher temperatures. These alloys are very promising for high temperature applications such as fire-resistant steels and in energy conversion systems, where long term retention of strength at elevated temperatures is a necessity.

### 7.1 Introduction

The theories and models of grain coarsening at high temperatures in polycrystalline materials are based on the principle of reduction of the total grain boundary area and, in turn, of the total energy of the system \([1, 2, 3, 4]\). In the case of 2-dimensional (2D) grain coarsening in isotropic microstructures, if the topology of the grains, and consequently, the curvature of the grain boundaries, is considered, the grains with six number of sides are stable, \( i.e. \), exhibit no change in volume, whereas the grains with the number of sides less than six shrink and the grains with the number of sides greater than six grow \([5, 6]\). In case a grain is surrounded by other grains smaller in size, topology dictates that the number of sides of the grain in question is always greater than six (and should grow) while the number of sides of a grain surrounded by other grains larger in size than itself has less than six sides (should shrink).

Recently, the 2D model of grain coarsening \([5, 6]\) has been extended to 3D by MacPherson and Srolovitz \([3]\). Based on the generalized von Neumann relationship in 3D derived by MacPherson and Srolovitz \([3]\), the number of faces (sides in 2D) for stable grains has been found to be equal to \( \sim 13.77 \) \([7]\), which is close to, but distinctly different from, other predictions in the literature between \( \sim 13.4 \) \([8, 9, 10, 11, 12]\) and \( \sim 13.56 \) \([13]\). In these references, simulations of grain coarsening predict that the grains with more than 13 faces should grow and the grains with less than or equal to 13 faces should shrink. Due to topological restraints, the grains surrounded by smaller grains (as compared to the central grain) always have more number of faces than the grains surrounded by larger grains. Thus, smaller grains in the vicinity of larger grains shrink and vice versa. In simple terms, the size of the grains can be directly related to the number of faces of the grains.

The number of faces \( (N_c) \) for grains, which are stable in volume (so called critical grains), between \( \sim 13.4 \) and \( \sim 13.8 \), is calculated assuming isotropic properties
of the grain boundaries \cite{7,8,9,10,11,12,13}, i.e., uniform energy of each grain boundary. This fixes the so-called exterior dihedral angle \cite{10}, \( \epsilon \), at edges to 60°. Glicksman et al. \cite{10} have investigated the case when \( \epsilon \) deviates from 60° due to the anisotropic properties of the grain boundaries. In their simulations, Glicksman et al. \cite{10} found that \( N_c \), the number of faces for the critical grain, varied between 40 and 4 as \( \epsilon \) was varied between \( \sim 23° \) and \( \sim 100° \) as compared to the ideal value of 13.397 for \( \epsilon = 60° \). This variation in \( N_c \) notwithstanding, the simulations still predicted that the grains with the number of faces less than \( N_c \) (read: small grains) have a positive mean curvature, i.e., will shrink, whereas the grains with the number of faces greater than \( N_c \) (read: large grains) have a negative mean curvature and will grow. In other words, large grains in a polycrystalline material should grow at the expense of small grains.

In this chapter, the validity of the aforementioned theories is examined using unique observations of grain coarsening in two Nb-containing iron-based alloys.

### 7.2 Materials and methods

#### 7.2.1 Materials

Two high purity alloys were manufactured from electrolytic (99.999% purity) ingredients using vacuum induction casting. The composition of the alloys is shown in Table 7.1. The casting process was carefully monitored in order to keep the concentration of impurities very low (<250 ppm for all other elements combined). One specimen of each alloy was made using electro-discharge machining (EDM) with the dimensions shown in Figure 7.1 in order to perfectly fit in the 3DXRD furnace described in Chapter 2 and Reference \cite{14}. The specimens had a change in diameter from 1 mm to 1.5 mm in the middle, which was used to define a reference by scanning with the X-ray beam. The composition of the specimens was determined using both EPMA and wet chemical analysis and no chemical heterogeneities were detected on the (sub)-micrometre level.

#### 7.2.2 3DXRD Experiments

The 3DXRD experiments were carried out at beam line ID11 of the European Synchrotron Radiation Facility (ESRF), Grenoble, France. Figure 7.2 shows the experimental setup. The specimens were placed in the 3DXRD furnace described in Chapter 2 and Reference \cite{14}. An S-type thermocouple was spot-welded to the
top of the specimen for accurate temperature control. The specimen chamber was purged with helium and sealed at a pressure of 0.4 atm. The X-ray beam (1200 µm wide and 300 µm high) was calibrated to 88.005 keV using the Laue–Laue setup. During each experiment, diffraction images were acquired from the specimen in two adjacent layers (see Figure 7.1) connected layers, each 300 µm high. For each layer, the furnace was rotated over a total angle of 11° (so-called sweep). Diffraction images were recorded using the FReLoN–4M detector during every 0.3° rotation with an exposure time of 0.2 s. These sweeps were repeated alternatingly for each layer during the experiments. This setup means that approximately every 126 s, a diffraction image was recorded at the same orientation of the specimen and in the
7.2. Materials and methods

Figure 7.2: Schematic showing the experimental setup. The dimensions are not to scale. The angles 2θ, ω, and η are defined.
same layer with respect to the incident beam. The rotation angle of 11° was chosen in order to have a good time resolution and to have all the grains in reflection at least once. The specimen to detector distance was chosen in such a way that four complete diffraction rings of the γ phase and three complete diffraction rings of the α phase were observed in the diffraction images. During each sweep, depending on the orientation of the grain, each grain diffracted either once or twice. At the beginning and the end of each isothermal annealing, the beam size was increased to 400 µm (wide beam) in the vertical direction in order to detect the grain located at the edges of the volume illuminated by the X-ray beam. These grains were detected later during data analysis by checking for grains, which show an increase in grain volume (in the sweep acquired using the wide beam) greater than 5% of the volume in the sweep just after (for the sweeps in the beginning of the isothermal annealing) or before (for the sweeps at the end of the isothermal annealing) the sweep acquired using the wide beam.

The aim of the experiments was to study the coarsening kinetics of γ grains during isothermal annealing. In total, isothermal annealing was carried out at three different temperatures each for 2.5 h and 2 h for the H-Nb and the L-Nb specimens, respectively. Before each isothermal annealing experiment, the specimens were heated to a temperature of 1150 °C for 5 min in order to dissolve any precipitates present in the material. It was later found, however, that in the case of the H-Nb alloy, NbC might be present up to 1200 °C. During the experiments, the specimens were heated to and cooled from the isothermal annealing temperature at heating / cooling rates equal to 1, 5 °C/min and 1, 2 °C/min during the phase transformation for the L-Nb and the H-Nb alloys, respectively. The heat treatments are shown in Figure 7.3.

### Table 7.1: Composition of the two alloys studied.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Mn</th>
<th>Nb</th>
<th>Fe</th>
<th>Nb:C ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-Nb</td>
<td>0.0099</td>
<td>0.98</td>
<td>0.10</td>
<td>balance</td>
<td>1.298</td>
</tr>
<tr>
<td>H-Nb</td>
<td>0.0097</td>
<td>0.97</td>
<td>0.86</td>
<td>balance</td>
<td>11.483</td>
</tr>
</tbody>
</table>

All the amounts are in wt%. The Nb:C ratio is the atomic ratio of Nb and C in the alloys.

#### 7.2.3 Data analysis method

The procedure described in Chapter 3 was followed in order to characterize diffraction spots from the raw images. Especially in case of the H-Nb specimen, where number of grains in the illuminated volume was large, the peak fitting routine
7.3 Results and discussion

proved to be of advantage in resolving overlapping peaks. A low threshold of 100 counts was used (background is around 100 counts as well). This threshold means that all grains with a volume greater than $\sim 50 \, \mu m^3$ ($\sim 2.3 \, \mu m$ radius) were detected. Furthermore, by matching displacement of position of diffraction spots in the two layers, diffraction spots arising from grains common to the two layers were detected and merged. The volume of the grains was calculated according to the procedure described in Chapter 4.

The grain size distribution, $P_v$ was calculated as the volume fraction of all grains in a volume interval divided by the volume of the corresponding interval.

Relative change in volume of the grains during annealing was calculated as follows: The relative change in the volume for a grain was calculated as:

$$\Delta V_{\text{grain}} = \begin{cases} \frac{(V_{\text{fin}} - V_{\text{init}})}{V_{\text{init}}} & \text{if } V_{\text{fin}} < V_{\text{init}} \\ \frac{(V_{\text{fin}} - V_{\text{init}})}{V_{\text{fin}}} & \text{otherwise} \end{cases} \tag{7.1}$$

where $V_{\text{init}}$ is volume of the grain at the beginning of isothermal annealing and $V_{\text{fin}}$ is volume of the grain at the end of isothermal annealing. All the grains were divided into 100 equally spaced categories in terms of initial grain radius. The average relative change in the volume ($\Delta V$) for all grains in each category was then calculated.

7.3 Results and discussion

In Chapter 5 the coarsening kinetics of $\gamma$ in a Fe–2wt% Mn alloy (Fe2Mn) were studied at a temperature of 1000 °C for more than 2 h. It was observed that the volume–averaged grain volume in the specimen increases by almost 10 times during the isothermal annealing (Figure 5.5). In this section, the results of coarsening kinetics of $\gamma$ in the L–Nb and the H–Nb alloys are presented.

Evolution of the volume–averaged grain size as a function of isothermal annealing time for the H–Nb and the L–Nb alloys at 960 °C, 1000 °C, 1100 °C and 1000 °C, 1050 °C, 1100 °C, respectively, are shown in Figure 7.4. Evolution of the volume–averaged grain size as a function of annealing time for the Fe2Mn alloy at 1000 °C, described in Chapter 5, is shown for comparison. It is remarkable that volume–averaged grain size in both the alloys at all annealing temperatures
7. Grain coarsening in Niobium containing steels studied by 3DXRD
Figure 7.3: Schematic of the heat treatments carried out on the L-Nb and the H-Nb specimens. The red ellipses highlight isothermal annealing at 1000°C, 1050°C and 1100°C in the L-Nb alloy and at 960°C, 1000°C and 1100°C in the H-Nb alloy.
remains (almost) constant during full duration of the isothermal annealing. This is in contrast to the characteristic behaviour of grain coarsening in metals, which normally resembles results for the Fe2Mn alloy, i.e., a continuously increasing grain size. The average grain size in the L–Nb alloy has more variations than the average grain size in the H–Nb alloy, even though both the alloys do not exhibit any significant increase in the average grain size as annealing progresses.

Figure 7.5 shows evolution of the $\gamma$ grain size distribution in the two layers in the L–Nb (a, b, c) and H–Nb (d, e, f) specimens as a function of isothermal annealing time. It is evident that for the H–Nb specimen, the grain size distribution appears to be static during the whole annealing time at all the three temperatures. For
Figure 7.5: Evolution of the γ grain size distribution as a function of annealing time. For the \( L - Nb \) alloy: (a) 1000 °C; (b) 1050 °C; (c) 1100 °C. For the \( H - Nb \) alloy: (d) 960 °C; (e) 1000 °C; (f) 1100 °C. The black squares, the red circles and the green triangles show the grain size distribution at 0 s, 2808 s and 7371 s, respectively during isothermal annealing in the two alloys.
7. Grain coarsening in Niobium containing steels studied by 3DXRD

![Graph showing grain size distribution evolution](image)

**Figure 7.6:** Evolution of the $\gamma$ grain size distribution in the Fe–2 wt% Mn alloy, described in Chapter 5, as a function of annealing time during isothermal annealing at 1000°C.

In the L–Nb case, relatively small changes in the grain size distribution during annealing are observed in Figure 7.5, although grains with volume less than $\sim 4 \times 10^5 \mu m^3$ exhibit smaller changes in $P_v$ than grains with larger volumes. These results are in contrast to the results for the Fe2Mn alloy, shown in Figure 7.6, where changes in the grain size distribution are more pronounced than in the case of the Nb–containing alloys. Interestingly, the behaviour of grains smaller than $\sim 4 \times 10^5 \mu m^3$, all reducing to very low volume fractions in Figure 7.6, is in contrast to the behaviour of the Nb–containing alloys in Figure 7.6. It is remarkable that even though Figure 7.5 shows that individual grains are not static during annealing, the average grain size, shown in Figure 7.4, is almost constant for the two Nb–containing alloys. The small variations in average grain size in Figure 7.4 are also reflected in changes in the grain size distribution, which are especially clear for the L–Nb alloy in Figure 7.5.
This means that there is interface motion, but without significant change in the average grain size. For the H–Nb alloy, no significant changes in the grain size distribution or the average grain size are observed.

To understand the reason behind the observed changes in the grain size distribution without significant variations in the average grain size, the average relative change in volume ($\Delta V$) as a function of the initial grain radius for the two alloys during isothermal annealing at the three annealing temperatures is plotted in Figure 7.7. Figure 7.7 (a–f) exhibit a unique feature: the smallest grains in the Nb–containing alloys have a net increase in the volume, whereas a significant number of the largest grains have a net decrease in the volume. Even though a number of grains with initial radius greater than $\sim 80 \, \mu m$ shrink to around 0.03 times their initial volume for the L–Nb alloy, none of these grains completely disappeared. Most of the shrinking grains in the H–Nb alloy exhibit a smaller change in volume as compared to the L–Nb alloy, confirming the variations in the grain size distribution shown in Figure 7.5 (d–f) and in the average grain size shown in Figure 7.4, which means that there was more interface motion in the L–Nb alloy than in the H–Nb alloy. Similar to the L–Nb alloy, the largest grains in the H–Nb alloy show a net decrease in the volume, even though the magnitude of the decrease is smaller for the H–Nb alloy than for the L–Nb alloy. To compare, the average relative change in volume as a function of the initial grain radius for the Fe2Mn alloy, described in Chapter 5, is shown in Figure 7.8. Confirming the results shown in Figure 7.6, large changes in grain volumes can be observed in Figure 7.8. The three main differences between the Fe2Mn alloy and the Nb–containing alloys, which can be deduced by comparing Figure 7.7 and Figure 7.8 are:

(i) A significant number of the grains ($\sim 1184$ out of 2385) in the Fe2Mn alloy disappeared, due to which, a number of markers for grains with radii less than $\sim 80 \, \mu m$ in Figure 7.8 are close to $-1$, which means complete disappearance of the grains. In comparison, less than 1% of the grains were observed to disappear during all of the experiments for the Nb–containing alloys.\(^1\)

(ii) Another important difference between Figure 7.7 and Figure 7.8 is the magnitude of the error bars, which correspond to the standard deviation from the mean $dV$. The magnitude of the error bars is substantially larger in the Fe2Mn alloy than in the Nb–containing alloys. Remarkably, one grain in the Fe2Mn specimen grew to

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\(^1\) All the grains, which were observed to disappear in the Nb–containing alloys, had volumes close to the detection limit of the technique. Thus, it is also possible that these grains fell below the threshold and did not disappear in reality.
Figure 7.7: Average relative change in the grain volume, $\Delta V$ (defined in Equation [7.1]), as a function of the initial grain radius in the Nb−containing alloys during isothermal annealing. The temperatures of annealing are: (a) 1000°C, (b) 1050°C and (c) 1100°C for the L−Nb alloy and (d) 960°C, (e) 1000°C and (f) 1100°C for the H−Nb alloy. Each marker shows $\Delta V$ for all the grains within a category defined by the initial grain radius, defined in §7.2.3. The colour of each marker corresponds to the number of grains in the corresponding category of the initial grain radius shown by the respective legend on the right. The error bars are equal to the standard deviation within each category.
7.3. Results and discussion

Figure 7.8: Average relative change in the grain volume, $\Delta V$ (defined in Equation 7.1), as a function of the initial grain radius in the Fe–2 wt% Mn alloy, described in Chapter 5, during isothermal annealing at 1000 °C. Each marker shows $\Delta V$ for all the grains within a category defined by the initial radius of the grains. The colour of each marker corresponds to the number of grains in the corresponding category of the initial grain radius shown by the colour legend on the right. The error bars are equal to the standard deviation within each category.

around 7000 times its volume at the beginning of the isothermal annealing. On the other hand, the largest change in volume for a grain in the Nb-containing alloys was for a grain, which grew to around 2.4 times its initial volume in the L–Nb alloy.

(iii) The third difference between the behaviour of $\gamma$ grains in the Fe2Mn alloy and the Nb-containing alloys is the behaviour of small grains. As can be seen in Figure 7.7, the grains with radii up to ~40 $\mu$m and up to ~15 $\mu$m for the L–Nb and the H–Nb specimens, respectively, show a net increase in the volume. In the
Fe2Mn specimen, however, most of the grains up to \( \sim 100 \, \mu m \) in radius show a net decrease in volume.

In order to investigate if NbC precipitates might be responsible for the retardation of \( \gamma \) coarsening kinetics, Thermo-Calc\textsuperscript{\textregistered} was used to calculate the dissolution temperatures of the precipitates (NbC for the L–Nb alloy and; NbC and Fe\(_2\)Nb for the H–Nb alloy). The results of Thermo-Calc\textsuperscript{\textregistered} are shown in Figure 7.9. It can be seen from Figure 7.9 that in the L–Nb alloy, NbC should not be present above \( \sim 1005 \, ^\circ C \), whereas in the H–Nb alloy, NbC should be present up to \( \sim 1200 \, ^\circ C \) and Fe\(_2\)Nb up to \( \sim 975 \, ^\circ C \). At 1000 \( ^\circ C \), in the L–Nb alloy, 0.0975 wt\% of Nb should still be present in solid solution out of the total 0.1 wt\% in the alloy. Thus, according to the Thermo-Calc\textsuperscript{\textregistered} calculations, although the presence of NbC precipitates might play a role in pinning the \( \gamma \) grain boundaries in the H–Nb case and in the L–Nb case (only at 1000 \( ^\circ C \), a very small volume fraction of precipitates), precipitates are not expected to be present at all in the L–Nb case at 1050 \( ^\circ C \) and 1100 \( ^\circ C \).

For the compositions of the Nb–containing alloys studied here, the accuracy of Thermo-Calc\textsuperscript{\textregistered} in calculating the dissolution temperatures of precipitates is questionable. However, the results shown in Figure 7.7 can be used as follows to (roughly) estimate whether precipitates are present or not at the temperatures studied:

The presence of precipitates in the L–Nb alloy at 1000 \( ^\circ C \) might be responsible for the observed decrease in the magnitude of the variations in the grain volumes (\( d\,V \)) as compared to the temperatures at which no precipitates are expected (1050 \( ^\circ C \) and 1100 \( ^\circ C \)). Thus, the lowest temperature at which no NbC precipitates are present in the L–Nb alloy should lie somewhere between 1000 \( ^\circ C \) and 1050 \( ^\circ C \). Furthermore, Figure 7.7 (d–f) show that the behaviour of the grains at the three temperatures (960 \( ^\circ C \), 1000 \( ^\circ C \) and 1100 \( ^\circ C \)) in the H–Nb alloys is the same and is comparable to the behaviour of the grains at 1000 \( ^\circ C \) in the L–Nb alloy (Figure 7.7 a). Thus, it is likely that precipitates were present in the H–Nb alloy at all the temperatures (960 \( ^\circ C \), 1000 \( ^\circ C \) and 1100 \( ^\circ C \)) studied in the present work. From the aforementioned discussion, it can be deduced that precipitates are not primarily responsible for the observed behaviour of grains (small grains grow while large grains shrink) and the formation of precipitates only reduces the rate of motion of the grain boundaries because the coarsening behaviour of small grains (Figure 7.7) and the evolution of the average grain size (Figure 7.4) are similar in the L–Nb alloy at all the temperatures (1000 \( ^\circ C \), 1050 \( ^\circ C \) and 1100 \( ^\circ C \)).
7.3. Results and discussion

Figure 7.9: Equilibrium mole fraction of the NbC and the Fe<sub>2</sub>Nb precipitates in (a) the L–Nb alloy and (b) the H–Nb alloy as a function of temperature calculated using Thermo–Calc®.
The theories of grain coarsening, see e.g. References [3, 7, 10], predict that grains with greater than or equal to 14 faces should grow while grains with less than 14 faces should shrink. In the experiments presented here, only the evolution of the size of the grains was recorded during isothermal annealing and the number of faces per grain cannot be calculated. However, the results of 500 random Voronoi tessellations, shown in Figure 7.10, show that the average number of faces is proportional to the radius of the grains. The standard deviation corresponds to the variations in the number of faces due to different sizes of the neighbouring grains.
Thus, the following discussion assumes that, on average, larger grains should have more number of faces as compared to smaller grains.

The observed net increase in volume for small grains in the Nb–containing alloys is opposite to the ‘normal’ grain growth observed in the Fe2Mn alloy and the theories of grain coarsening, which predict that large grains should grow at the cost of small grains. The markers in Figure 7.8 have a minima at grain radius $\sim 40 \mu m$, which means that the rate of shrinkage is highest for grains with radius $\sim 40 \mu m$ and the smallest grains in the sample do not shrink as fast. This is consistent with the results described in References $[9, 10, 11]$ that the highest rate of shrinkage is for grains with $\sim 6$ faces (as compared to $N_c = 13.397$ for stable grains) and the grains with number of faces less than $6$ shrink at a slower rate.\footnote{Even though it is not possible to directly correlate the number of faces with the size of the grains (since the exact number of faces will depend on the size of neighbouring grains), as described in the text, the average number of faces for grains should increase as the grain size increases.}

Figure 7.7 shows that small grains in the Nb–containing alloys grow and large grains shrink, thereby resulting in an (effective) increase in the total interface area of the system. Furthermore, almost none of the grains in the alloys were observed to disappear. A possible explanation for such behaviour is as follows:

To describe grain coarsening at high temperatures, most theories only consider the movement of grain boundaries in order to reduce the total grain boundary area and, in turn, the total energy of the system $[1, 2, 4]$. The effect of segregation of solute atoms to the grain boundaries is most often incorporated as solute drag $[16, 17, 18]$. However, in the case of nano-crystalline materials, the Gibbs free energy balance between the solute atoms segregating to grain boundaries and the energy contribution of the grain boundaries has been investigated $[19, 20, 21]$. In the following discussion, this balance of Gibbs free energy and its influence on grain coarsening in the Nb–containing alloys is investigated.

According to the Gibbs interface equation $[21]$, both the energy of the grain boundaries and the total energy of the system are lowered due to the segregation of solute atoms to the grain boundaries. In case the total grain boundary area changes, the change in the energy of the system ($dG$) is $[21] \footnote{This treatment assumes a uniform energy of the grain boundaries.}$

$$dG = \left(\sigma - \Gamma \bar{G}_s\right) dA \quad (7.2)$$
where \( \sigma \) is the grain boundary energy per unit area, \( \Gamma \) is the excess amount of the solute at the boundaries, \( \bar{G}_s \) is the Gibbs free energy of segregation per solute atom and \( dA \) is the change in the grain boundary area of the system. In all the cases where \( \sigma < \Gamma \bar{G}_s \), an increase in the total grain boundary area (\( dA > 0 \)) leads to a reduction in the total energy of the system.

Maruyama et al. [22] have observed strong segregation of Nb to grain boundaries in B.C.C.−iron (\( \alpha \)), with \( \Gamma_{\alpha} = 1.6 \times 10^{-6} \text{ mol/m}^2 \). In the case of isothermal annealing at 960 °C, \( \bar{G}_{s,\alpha} = 43.6 \text{ kJ/mol} \). Thus, in the case of \( \alpha \)−iron, the maximum grain boundary energy, \( \sigma_{c,\alpha} \), for which an increase in the total grain boundary area can reduce the total energy of the system is \( \sigma_{c,\alpha} = 0.069 \text{ J/m}^2 \). Unfortunately, no studies have been carried out on the segregation of Nb to grain boundaries in \( \gamma \)−iron.

Assuming that, similar to the case of the segregation of Si to grain boundaries in \( \alpha \)−iron and \( \gamma \)−iron, the segregation of Nb to grain boundaries in \( \gamma \)−iron should be around 7 times higher than the segregation of Nb to grain boundaries in \( \alpha \)−iron, \( \Gamma_{\gamma} = 1.1 \times 10^{-5} \text{ mol/m}^2 \) and \( \bar{G}_{s,\gamma} = \bar{G}_{s,\alpha} \), \( \sigma_{c,\gamma} \) is found to be 0.49 J/m^2. Given this high value of \( \sigma_{c,\gamma} \) and that, according to the Gibbs interface equation, \( \sigma \) is lowered due to segregation of solute atoms to the grain boundaries, the situation where the energy of the grain boundaries (\( \sigma \)) in a material with segregation of Nb atoms to the \( \gamma \)−\( \gamma \) grain boundaries is lower than \( \sigma_{c,\gamma} \) is possible. Thus, in such systems, at high temperatures, the material would not reduce the total grain boundary area, but increase it and still lower the total energy of the system. The only possibility to increase the total grain boundary area in a single phase material is by growth of small grains at the cost of large grains (similar to the results in Figure [7.7] for the Nb−containing alloys) because nucleation of new grains in the single phase material would not be possible.

The segregation of Mn to grain boundaries in \( \gamma \)−iron has been observed to be weaker [24] as compared to the segregation of Nb to grain boundaries in \( \alpha \)−iron, and consequently, significantly weaker than the segregation of Nb to grain boundaries in \( \gamma \)−iron. For Mn, \( \sigma_{c,\alpha} = 2.6 \times 10^{-3} \text{ J/m}^2 \), using \( \Gamma_{\alpha,Mn} \approx 0.4 \cdot \Gamma_{\alpha,Nb} \) [22] [24] and \( \bar{G}_{s,\gamma} = 8 \text{ kJ/mol} \) [25]. Thus, the segregation of Mn atoms to the grain boundaries in the Fe2Mn alloy should have negligible influence on grain coarsening (not considering solute drag) and coarsening is governed by reduction in the total grain boundary area of the system.

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7.4 Conclusions

Unique results of the coarsening of $\gamma$ grains during isothermal annealing are presented for two Nb-containing alloys with Nb:C atomic ratios greater than unity (1.3:1 and 11.5:1). The alloys were annealed isothermally at three temperatures each: 1000 °C, 1050 °C and 1100 °C for the low Nb alloy and 960 °C, 1000 °C and 1100 °C for the high Nb alloy.

During the isothermal annealing experiments, no significant changes in the average grain size were observed at temperatures up to 1100 °C. Inspection of the grain size distribution and relative changes in the grain volumes of individual grains revealed that, unlike the average grain size, the volume of individual grains was not constant during annealing. Increase in the volume of small grains (less than $\sim 40 \mu m$ and $\sim 15 \mu m$ in radius for the low Nb and the high Nb alloys, respectively) whereas reduction in the volume of larger grains was observed. Interestingly, almost all the grains in the alloys were present at the end of isothermal annealing. The results are contrasted with ‘normal’ grain coarsening in a Fe–2 wt% Mn alloy, shown in Chapter 5. Preferential segregation of Nb atoms to grain boundaries is proposed as a possible explanation for the observations.

The alloys designed and studied here exhibit very unique combination of properties: the possibility of achieving small $\gamma$ grain size during heating and limited or no grain coarsening (average grain size) at temperatures up to 1100 °C. These alloys are very promising for high temperature applications such as fire-resistant steels and energy conversion systems, where long term retention of strength at elevated temperatures is a necessity.

7.5 Bibliography


7. Grain coarsening in Niobium containing steels studied by 3DXRD


Summary

The mechanical properties of metals depend strongly on the microstructure. Three processes, which determine the resulting microstructure during thermo-mechanical processing of metals, are: (i) grain nucleation and grain growth during phase transformations; (ii) grain coarsening at high temperatures and; (iii) deformation characteristics including recrystallization. Understanding the evolution of ferrite-to-austenite ($\alpha \rightarrow \gamma$) phase transformation and coarsening of $\gamma$ grains at high temperatures is very important for various applications such as fire-resistance and energy conversion systems. The aim of this thesis is twofold: (i) to develop the Three-Dimensional X-Ray Diffraction (3DXRD) technique further in order to investigate the evolution of the microstructure of polycrystalline materials at high temperatures and; (ii) to demonstrate the possible advances, which can be made towards better understanding of the fundamental processes of nucleation and grain coarsening in iron-based alloys. In view of this, the thesis is divided into two parts: Chapters 2, 3 and 4 outlining the advances made in the experimental technique and Chapters 5, 6 and 7 describing the materials science results obtained for iron-based alloys.

Chapter 2 describes a multi-purpose furnace designed for studies using synchrotron radiation on polycrystalline materials, namely metals, ceramics and (semi-)crystalline polymers. The furnace has been designed to carry out 3DXRD measurements, but can also be used for other types of synchrotron radiation research. The furnace has a very low thermal gradient across the specimen ($< 0.2^\circ$C/mm). A thermocouple welded to the specimen is used to accurately determine the temperature. The furnace can be rotated over an angle of 90° in order to determine the crystallographic orientation and the position of each individual grain. It is possible to follow the growth kinetics of all the grains in the illuminated volume of the specimen. The specimen environment can be controlled varying from vacuum (up to $10^{-5}$ mbar) to gas or air filled. The maximum temperature of operation is 1500 °C, with the possibility of achieving high heating (up to 20 °C/s) and cooling rates (up to 30 °C/s without quenching gas). 3D maps of the microstructure of the specimen can be generated at elevated temperatures by bringing a high-resolution detector close to the specimen. An example of a simulation of the heat affected zone during the thermal cycle of a weld in a TRIP steel carried out using the furnace is shown. The unique characteristics of the furnace open the possibility of new fields of research in materials science using synchrotron radiation.
Chapters 3 and 4 describe a framework developed for analysis of data acquired using 3DXRD. The classical techniques for analysis of 3DXRD data are limited up to only a thousand grains or so. In order to determine characteristics of more grains, the usual strategy is to scan the sample at multiple locations by the X-ray beam, thereby reducing the time resolution of the experiments. The framework presented in this thesis is shown to handle more than 3000 grains and is very useful to study statistically representable number of grains with high time resolution.

In Chapter 3, a procedure for pre-processing of the data acquired using 3DXRD is presented. The procedure deals with pre-processing of the data for input in the algorithms presented in Chapter 4 for the determination of grain characteristics. An algorithm is presented for accurate identification of overlapping diffraction peaks from X-ray diffraction images, which has been a long-standing issue for experiments of this type. The algorithm works in two stages, namely, identification of overlapping peaks by using a seeded-watershed algorithm and then fitting the peaks with a pseudo-Voigt shape function to yield accurate centre-of-mass position and integrated intensity of the peaks. Regions consisting of up to six overlapping peaks can be successfully fit. Two simulations are used to verify the results of the algorithms. An example of processing of diffraction images acquired with a specimen consisting of more than 1600 grains is shown. Furthermore, a description of a procedure for the determination of the global parameters of the experiments without the need of a calibration specimen is described and validated using simulations. This is immensely beneficial in simplifying the experiments and the subsequent data analysis.

Chapter 4 describes procedures for the determination of grain characteristics of undeformed grains for data acquired using 3DXRD. The developed approaches are orders of magnitude faster than the presently available approaches for processing of thousands of grains. Using the information obtained from the steps described in Chapter 3 the volume, the crystallographic orientation, the centre-of-mass position and the strain stage of the grains in the illuminated volume can be determined. The algorithms dealing with the determination of the crystallographic orientation, centre-of-mass position and strain state of the grains are divided into two parts: first dealing with indexing, that is, assigning the diffraction spots to individual grains and the second dealing with the refinement of the crystallographic orientation, centre-of-mass position and strain state of the grains using the diffraction spots assigned during indexing. The presently available approaches to indexing that exist in literature are presented and compared with the approaches developed here. Two novel approaches to indexing are developed:
For large numbers of grains, the first approach to indexing employs a novel specimen 'surface' scanning technique in combination with a reduced number of search orientations to achieve high robustness and computation efficiency. On the other hand, for data acquired using small number of grains in the specimen volume illuminated by the X-ray beam, the position of the diffracting grains in the specimen is neglected during indexing for considerable speedup. For unstrained specimens, both the modes of indexing and the subsequent process of refinement are validated using simulated data for 60 and 3000 grains. In both the cases, the centre-of-mass position of the grains was determined with a mean error of 0.7 \( \mu \text{m} \) and the orientation was determined with a mean error of 0.0003\(^\circ\). Furthermore, an experiment is 'mimicked' by introducing experimental errors in the simulation for 3000 grains. The resulting mean errors in centre-of-mass position (2.1 \( \mu \text{m} \)) and orientation (0.008\(^\circ\)) of the grains are higher than the errors for the ideal simulations and the errors in an experiment will depend on the experimental errors. The algorithms dealing with strained specimens are validated using a simulation for 3000 grains with 'mimicked' experimental errors. The centre-of-mass position, the crystallographic orientation, the normal strain tensor components and the shear strain tensor components of the grains were determined with a mean error of 8 \( \mu \text{m} \), 0.006\(^\circ\), 5.2 \( \times \) 10\(^{-5}\) and 2.8 \( \times \) 10\(^{-5}\), respectively.

Further building up on the indexing approach using a 'surface' scanning technique, an advanced indexing approach using the symmetric properties of Friedel pairs is developed. The approach uses both symmetric and asymmetric Friedel pairs to reduce the search surface in the specimen to a straight line for each possible Friedel pair. This allows for a speed up of around 40 times during computation. Indexing of the 3000 grains simulation shows that highly accurate results can be obtained in minutes. Furthermore, the first results of indexing of experimental data acquired from a specimen consisting of more than 2200 grains in the illuminated volume are shown.

In Chapter 5, the results of study of grain coarsening of \( \gamma \) at 1000 \( ^\circ \text{C} \) in a binary Fe–2 wt% Mn alloy using 3DXRD are presented. The evolution of volume, average crystallographic orientation and mosaicity of more than 2000 individual \( \gamma \) grains was tracked during annealing. It was found that there exists an approximately linear relationship between grain size and mosaicity, which means that orientation gradients are present in the grains. The orientation gradients remain constant during coarsening and consequently the character of grain boundaries changes during coarsening, affecting the coarsening rate. Furthermore, changes in the average orientation of grains during coarsening were observed. The changes could
be understood by taking the observed orientation gradients and anisotropic movement of grain boundaries into account. Five basic modes of grain coarsening were deduced from the measurements, which include: anisotropic (I) and isotropic (II) growth (or shrinkage); movement of grain boundaries resulting in no change in volume but change in shape (III), movement of grain boundaries resulting in no change in volume and mosaicity, but change in crystallographic orientation (IV); and no movement of grain boundaries (V).

Chapter 6 elaborates unique measurements in order to understand the effect of special orientations relationships between the nuclei and the matrix grains on the process of nucleation. Nucleation of γ grains in an Fe–C–Mn–Ti alloy during step-wise heating (2 °C/step) was studied by 3DXRD. At all temperatures during the transformation, new γ nuclei were observed to appear and the number of γ nuclei per unit untransformed volume increased rapidly with increasing temperature. The total number of γ nuclei was almost 1.4 times the total number of α grains before the transformation. A number of γ grains in the specimen (as large as 120 µm in diameter) were consumed by other γ grains during the phase transformation. The overall Ψ parameter for all the γ nuclei, which represents the effects of the shape of the nucleus and the interfacial energies, was found to be similar to what has been reported before for the α → γ phase transformation (2.9 – 4.6 × 10⁻⁸ J m⁻⁶). The K–S orientation relationship (OR) was found to be more abundant than the N–W OR for the γ nuclei. Furthermore, close— to ideal N–W OR was detected less frequently than close— to ideal K–S OR. Around 93% of the γ nuclei had a either N–W or K–S OR with at least one of the neighbouring α grains. More than half of the γ nuclei had a special OR with two or more α neighbours. It was surprising that the frequency of occurrence of γ nuclei having a special OR with three and four α neighbours was high, indicating the presence of a very special microstructure. A high nucleation rate of α grains having special ORs with the parent γ grain during cooling coupled with minimal coarsening of the α grains is proposed as a possible mechanism of the formation of this special microstructure. The Ψ parameter was divided into five categories based on the number of α neighbours with a special OR. The γ grains having special ORs with four α neighbours have the lowest value of Ψ, followed, in order, by γ grains having special ORs with three, two and one α neighbours. This means that the nucleation rate is highest for the γ grains having special ORs with four α neighbours. The γ grains nucleating without a special OR with any of the α neighbours appear towards the end of the phase transformation. These observations are instrumental for a better understanding of the crucial phenomenon of nucleation during phase transformations in polycrystalline materials.
Chapter 7 describes the results of grain coarsening kinetics of γ grains in alloys containing Nb with Nb:C ratios greater than unity (1.3:1 and 11.5:1) studied in situ using 3DXRD. The alloys were annealed isothermally at three temperatures each: 1000 °C, 1050 °C and 1100 °C for the low Nb alloy and 960 °C, 1000 °C and 1100 °C for the high Nb alloy. The results of isothermal annealing revealed a very interesting behaviour: almost no significant change in the average γ grain size in the alloys at temperatures up to 1100 °C for durations greater than 2 h. However, changes in grain volume at the level of individual grains were observed. Almost none of the grains in the specimens disappeared during the isothermal annealing. These results are in contrast with ‘normal’ grain coarsening behaviour of a Fe–2 wt% Mn alloy shown in Chapter 5. Strong segregation of Nb atoms to grain boundaries is proposed as a possible mechanism for the observations. The alloys designed and studied here exhibit very unique combination of properties: the possibility of achieving small γ grain size during heating and limited or no grain coarsening (average grain size) at temperatures up to 1100 °C. These alloys are very promising for high temperature applications such as fire–resistant steels and energy conversion systems, where long term retention of strength at elevated temperatures is a necessity.
Samenvatting

De mechanische eigenschappen van metalen hangen sterk af van de microstructuur. De drie processen die de uiteindelijke microstructuur bepalen tijdens thermisch–mechanisch bewerken van metalen, zijn: (i) de vorming en groei korrels tijdens fase transformaties; (ii) korrelvergroving op hoge temperaturen en; (iii) deformatiekarakteristieken, inclusief rekristallisatie. Het begrijpen van de fase transformatie ($\alpha \rightarrow \gamma$) van ferriet ($\alpha$) naar austeniet ($\gamma$) in staal en de groei van de $\gamma$–korrels op hoge temperaturen is erg belangrijk voor diverse toepassingen, zoals de ontwikkeling van vuur–bestendig staal en staal voor energie conversie systemen die op hoge temperatuur functioneren. Het doel van dit proefschrift is tweeledig: (i) om de drie dimensionale röntgen diffractie (3DXRD) techniek verder te ontwikkelen, zodat het mogelijk wordt om de evolutie van de microstructuur van polykristallijne materialen op hoge temperaturen te onderzoeken; (ii) om te laten zien op welke wijze meer inzicht kan worden verkregen in fundamentele processen als kiemvorming en korrelgroei in legeringen gebaseerd op ijzer.

Hoofdstuk 2 beschrijft een multifunctionele oven, die is ontworpen voor studies die gebruik maken van synchrotronstraling voor het bestuderen van polykristallijne materialen, zoals metalen, keramische materialen en (deels) kristallijne polymeren. De oven is ontworpen voor gebruik tijdens 3DXRD metingen, maar kan ook worden gebruikt voor andere synchrotron-technieken. De oven heeft een erg lage temperatuursgradient over het preparaat ($< 0.2^\circ$ C/mm). Een thermokoppel dat aan het preparaat is gelast wordt gebruikt om de temperatuur nauwkeurig te bepalen. De oven kan over een hoek van 90° roteren om de kristallografische oriëntatie en het zwaartepunt van elke individuele korrel in het materiaal te bepalen. Het is mogelijk om de groeikinetiek van alle korrels te volgen in het aangestraalde volume van het preparaat. De atmosphere in de oven kan worden ingesteld en kan worden gevarieerd van vacuüm (tot $10^{-5}$ mbar) tot gas met een kleine onderdruk. De maximale werktemperatuur is 1500 °C, met de mogelijkheid van hoge opwarmsnheden (tot 20 °C/s) en afkoel snelheden (tot 30 °C/s zonder koelgas, met koelgas zijn de afkoelsnelheden hoger). Er kunnen 3D-reconstructies van de microstructuur van het preparaat worden gemaakt op hoge temperaturen door de hoge–resolutie detector in dicht (7 mm) in de buurt van het preparaat te brengen. Een voorbeeld
van het gebruik van de oven wordt gegeven, waarbij de warmte beïnvloede zone wordt gesimuleerd tijdens de thermische cyclus van een las in een TRIP staal. De unieke eigenschappen van de oven openen nieuwe onderzoeksmogelijkheden voor het bestuderen van polykristallijne materialen m.b.v. synchrotron straling.

Hoofdstukken 3 en 4 beschrijven een raamwerk dat is ontwikkeld voor de analyse van gegevens die zijn verkregen met 3DXRD. De klassieke technieken voor de analyse van 3DXRD data zijn gelimiteerd tot ongeveer 1000 korrels. De gebruikelijke strategie om de karakteristieken van duizenden korrels bepalen, is om het preparaat met de röntgenbundel op meerdere locaties te scannen, met als gevolg dat de tijdresolutie van de experimenten afneemt. Het in dit proefschrift gepresenteerde raamwerk kan meer dan 3000 korrels aan en is zeer nuttig om een statistisch relevant aantal korrels met een hoge tijdresolutie te bestuderen.

In hoofdstuk 3 wordt een procedure gepresenteerd voor pre-processing van 3DXRD data. De procedure betreft pre-processing van data die gebruikt wordt als invoer voor algoritmes voor het bepalen van de karakteristieken van korrels die gepresenteerd worden in hoofdstuk 4. Een algoritme wordt gepresenteerd voor nauwkeurige bepaling van overlappende diffractiepieken, hetgeen een slepende kwestie is voor dit soort experimenten. Het algoritme werkt in twee fasen: identificatie van overlappende pieken met behulp van een ‘seeded watershed’ algoritme en vervolgens het fitten van de pieken met een pseudo-voigt functie voor een nauwkeurige bepaling van de positie en geïntegreerde intensiteit van de pieken. Regio’s bestaande uit maximaal zes overlappende pieken kunnen met succes worden gefit. Twee simulaties zijn gebruikt om de algoritmen te verifiëren. Er wordt een voorbeeld gegeven van het verwerken van diffractiebeelden, die zijn verkregen met een preparaat bestaande uit meer dan 1600 korrels. Daarnaast wordt een procedure beschreven voor de bepaling van de globale parameters van experimenten zonder de noodzaak van het meten aan een calibratie-preparaat. Deze procedure is gevalideerd met behulp van simulaties. Dit is heel gunstig voor de vereenvoudiging van de experimenten en de daarop volgende data-analyse.

Hoofdstuk 4 beschrijft procedures voor de bepaling van kenmerken van ongedeformeerde korrels uit 3DXRD data. De hier ontwikkelde aanpak is ordes van grootte sneller dan de momenteel beschikbare benaderingen voor verwerking van duizenden korrels. Met behulp van de informatie die is verkregen uit de stappen die zijn beschreven in hoofdstuk 3 kunnen het volume, de kristallografische oriëntatie, het zwaartepunt en de spanningstoestand van de korrels in het aangestraalde volume worden bepaald. De algoritmen voor de bepaling van de kristallografische
oriëntatie, het zwaartepunt en spanningstoestand van de korrels zijn verdeeld in
 twee delen: ten eerste indexeren, dat wil zeggen, het toewijzen van de diffractie
 pieken aan individuele korrels en ten tweede een verfijning van de kristallografis-
 che oriëntatie, het zwaartepunt en spanningstoestand van de korrels met behulp
 van de diffractie pieken toegewezen tijdens het indexeren. De momenteel in de
 literatuur beschikbare benaderingen voor het indexeren worden gepresenteerd en
 vergeleken met de benadering ontwikkeld in dit proefschrift. Er zijn twee nieuwe
 benaderingen voor indexeren ontwikkeld. De eerste benadering, voor het index-
 eren van grote aantallen korrels, behelst het scan van een 'oppervlak' in het
 preparaat in combinatie met het zoeken naar een beperkt aantal oriëntaties om zo
 een hoge robuustheid en efficiëntie te bereiken.

Anderzijds wordt, voor data verkregen met een klein aantal korrels in het aange-
 straalde volume van het preparaat, de positie van de diffracterende korrels in het
 preparaat verwaarloosd tijdens het indexeren om zo te komen tot een aanzienlijke
 snelheidswinst. Voor spanningsvrije preparaten zijn beide vormen van indexeren
 en het daaropvolgende proces van verfijning gevalideerd met gesimuleerde data
 met 60 en 3000 korrels. In beide gevallen is het zwaartepunt van de korrels bepaald
 met een gemiddelde fout van 0.7 micrometer en de oriëntatie bepaald met een
 gemiddelde fout van 0.0003°. Daarnaast is een experiment 'nagebootst' door de
 invoering experimentele fouten in de simulatie met 3000 korrels. De resulterende
 gemiddelde fouten in het zwaartepunt (2.1 micrometer) en oriëntatie (0.008°) van
 de korrels zijn hoger dan de fouten voor de ideale simulaties en de fouten in een
 experiment zullen afhangen van de experimentele fouten. De algoritmen voor
 vervormde preparaten worden gevalideerd met behulp van een simulatie met 3000
 korrels met 'nagebootste' experimentele fouten. Het zwaartepunt, de kristallografis-
 che oriëntatie, de normale component van de rektensor en de afschuif-component
 van de rektensor van de korrels zijn bepaald met een gemiddelde fout van re-
 spectievelijk 8 micrometer, 0.006°, 5.2 × 10⁻⁵ en 2.8 × 10⁻⁵.

Door verder te bouwen op de benadering voor indexeren waarbij gebruik gemaakt
 wordt van de 'oppervlak scan techniek', is een geavanceerde aanpak voor index-
 eren ontwikkeld met behulp van de symmetrische eigenschappen van Friedel-
paren. De aanpak maakt gebruik van zowel de symmetrische als de asymmetrische
 Friedel paren om het oppervlak in het preparaat te beperken tot een rechte lijn
 voor elk mogelijks Friedel pair. Dit maakt de berekening ongeveer 40 keer sneller.
 Uit het indexeren van de '3000 korrels simulatie' blijkt dat in een paar minuten zeer
 nauwkeurige resultaten kunnen worden verkregen. Bovendien worden de eerste
 resultaten getoond van het indexeren van experimentele gegevens verkregen uit
Samenvatting

Een preparaat met meer dan 2200 korrels in het aangestraalde volume.

In hoofdstuk 5 worden de resultaten gepresenteerd van een studie naar vergroETING van $\gamma$-korrels bij 1000 °C in een binaire Fe–2 gew.% Mn legering gebruik makend van 3DXRD. De evolutie van het volume, de gemiddelde kristallografische oriëntatie en de oriëntatiespreiding van meer dan 2000 individuele korrels is gevolgd tijdens gloeien. Het bleek dat er bij benadering een lineair verband bestaat tussen de korrelgrootte en oriëntatiespreiding, wat betekent dat er oriëntatiegradiënten aanwezig zijn in de korrels. De oriëntatiegradiënten blijven constant tijdens vergroving en dus verandert het karakter van korrelgrenzen tijdens vergroving, hetgeen effect heeft op de snelheid van vergroving. Bovendien zijn veranderingen in de gemiddelde oriëntaties van korrels tijdens vergroving waargenomen. De veranderingen kunnen worden verklaard door rekening te houden met de waargenomen oriëntatiegradiënten en anisotrope beweging van korrelgrenzen. Vijf basis modi van korrel vergroving zijn afgeleid uit de metingen, waaronder: anisotrope (I) en isotrope (II) groei (of krimp); verschuiving van korrelgrenzen zonder verandering in volume van de korrel maar met verandering van vorm van de korrel (III), verschuiving van korrelgrenzen zonder verandering in volume of oriëntatiespreiding, maar met verandering van kristallografische oriëntatie (IV); geen beweging van korrelgrenzen (V).

Hoofdstuk 6 gaat in op unieke metingen om het effect van speciale oriëntatie relaties tussen de kiemen en de matrix korrels op kiemvorming te begrijpen. Kiemvorming van $\gamma$-korrels is bestudeerd met 3DXRD in een Fe–C–Mn–Ti legering tijdens stapsgewijze verwarming (2 °C/stap). Bij alle temperaturen tijdens de transformatie zijn nieuwe kiemen waargenomen en het aantal kiemen per ongetransformeerd volume nam snel toe met toenemende temperatuur. Het aantal kiemen was bijna 1.4 maal het totale aantal korrels voor de transformatie. Een aantal korrels in het preparaat (met een grootte van 120 micron in diameter) werden ‘opgegeten’ door andere korrels tijdens de fase transformatie. De globale $\Psi$ parameter voor alle kiemen die de effecten van kiemvorm en grensvlakkenenergie vertegenwoordigt, bleek vergelijkbaar met hetgeen eerder gerapporteerd is voor de $\gamma \rightarrow \alpha$ fasetransformatie ($2.9 - 4.6 \times 10^{-8} \text{ J}^3 \text{m}^{-6}$). De K-S oriëntatierelatie (OR) kwam meer voor dan de N-W OR voor de $\gamma$-kiemen. Bovendien werd ‘bijna ideale’ N-W OR minder vaak gedetecteerd dan ‘bijna ideale’ K-S OR. Ongeveer 93% van de kiemen hadden ofwel een N-W OR of een K-S OR met ten minste één van de naburige $\alpha$ korrels. Meer dan de helft van de kiemen had een speciale OR met twee of meer $\alpha$ buren. Het was verrassend dat de frequentie van $\gamma$-kiemen met een speciale OR met drie of vier $\alpha$ buren hoog was, wat duidt op de aanwezigheid van een zeer speciale microstructuur. Een hoge
kiemvormingssnelheid van α korrels met een speciale OR met de ‘ouder’ γ-korrel tijdens afkoelen in combinatie met minimale vergroting van de γ korrels wordt voorgesteld als mogelijk mechanisme voor de vorming van deze bijzondere microstructuur. De Ψ-parameter is onderverdeeld in vijf categorieën gebaseerd op het aantal α buren met een speciale OR. De γ korrels die een speciale ORs hebben met vier α buren hebben de laagste waarde voor Ψ, gevolgd door, in volgorde, γ korrels die een speciale ORs hebben met drie, twee en één α buren. Dit betekent dat de kiemvormingssnelheid het hoogste is voor de γ korrels die een speciale OR met vier α buren hebben. De γ korrels die kiemen zonder een speciale OR met één van de α buren, verschijnen aan het einde van de fase transformatie. Deze waarnemingen zijn essentieel voor een beter begrip van het cruciale fenomeen kiemvorming tijdens fase transformaties in polykristallijne materialen.

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Acknowledgements

*Life is like a train journey. Some people leave while we are travelling and we disembark while some others are travelling.*

H.H. Shri Bhola Nathji Bhagwan.

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With tears in my eyes, I bid adieu to the Netherlands
I hope not forever
Hemant
List of Publications


10. Dere, E. G., Sharma, H., Offerman, S. E., and Sietsma, J. The effect of NbC precipitates and Nb in solid-solution on the phase transformation kinetics
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