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Influence of Heat Treatment Parameters on Phase Transformations in the Near-Beta Titanium Alloy Ti-1Al-8V-5Fe

A thesis submitted in fulfilment of the requirements for the award of the degree

Doctor of Philosophy

from

University of Wollongong

by

Dipl.-Ing. Lisa Thönnessen

Department of Engineering and Information Sciences

November 2017
Abstract

This research aims to combine in-situ diffraction techniques with transmission electron microscopy to answer open questions with respect to phase transformations in near-β titanium alloys. The exact mechanism of the β- to ω-phase transformation was determined in a Ti-1Al-8V-5Fe alloy. Specific attention was paid to the role the ω-phase plays in subsequent α-phase precipitation.

Specimens were heated to α-precipitation temperatures between 763 and 823 K at rates of 1 to 100 K/min in-situ in high-energy X-ray, neutron and electron diffraction facilities. In addition, an isothermal holding time at 623 K was imposed in some experiments. These in-situ techniques provided insights into the exact sequence of phase transformations as well as the kinetics of transformation as influenced by the selected heat treatments. Selected specimens were prepared for ex-situ electron microscopy investigations, which shed further light on the mechanisms of the pertaining phase transformation at atomic level.

These investigations revealed that the extent of solute diffusion plays a major role in determining the phase transformation sequence and hence, α-nucleation kinetics and morphology.

Experimental conditions that promote a high degree of solute diffusion, such as heating rates of less than 5 K/min or holding at 623 K, lead to full β- to ω-phase transition. The ω-phase precipitates as small, homogeneously distributed particles and of hexagonal crystal structure. Such a microstructure provides the ideal conditions for α-phase formation at elevated temperatures by enhancing α-phase nucleation kinetics. Under these conditions α-phase nucleation will initiate below 700 K. The α-precipitates nucleate on ω-precipitates and grow to consume them, thereby producing a microstructure that consists of fine α-precipitates, homogeneously distributed through the β-matrix and of a composition close to equilibrium.

Conversely, heating cycles that significantly limit the extent of solute diffusion, such as heating at a rate of 100 K/min, lead to incomplete β- to ω-phase transition. In this instance the ω-phase precipitates are not of hexagonal crystal structure and in
addition, only a small fraction of these \(\omega\)-precipitates form. Such heat treatments lead to a delay in the subsequent \(\alpha\)-phase precipitation kinetics, to the extent that \(\alpha\)-phase nucleation only occurs at 823 K. The primary \(\alpha\)-precipitates formed under these conditions are coarse, but small secondary \(\alpha\)-precipitates also form and hence, an inhomogeneous microstructure results.

The improved understanding of microstructural development, specifically the link between thermo-mechanical parameters and the resulting microstructure of a Ti-1Al-8V-5Fe alloy, gained through this study should lead to an improved ability to tailor the mechanical properties of products in industrial practice. The findings outlined in this thesis contribute to a better understanding of the scientific principles underpinning the phase transformation mechanisms in near-\(\beta\) titanium alloys. Moreover, in addition to making a contribution to science it is envisaged that a better foundation for an improved design of products manufactures from Ti-10V-2Fe-3Al and related alloys have been laid.
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Lisa Thönnessen

Wollongong, November 2017
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Introduction

Fine tuning the properties of titanium alloys will be a major challenge for future lightweight structural applications in the aerospace industry. Microstructural control through thermo-mechanical processing (Tmp) is an effective way of achieving superior mechanical properties in these types of alloy. For near-β-titanium alloys the formation and precipitation of α-phase represents the property determining step within the tmp route. (Jones & Jackson 2011, p. 250-252).

Fine-scale α-precipitates will form during cold rolling and low temperature annealing, leading to an improvement in the mechanical properties. The volume fraction, size and distribution of these α-precipitates highly depend on processing parameters such as heating rate, holding temperature and deformation conditions. Nucleation of α-phase can occur at dislocations, vacancies, grain boundaries, or at another phase, such as the ω-phase. The role of ω-precipitates on the nucleation of α- in the β-phase of titanium alloys is still not well understood. (Jones et al. 2009). To control the microstructure during the processing, it is very important to have knowledge about the thermodynamics and kinetics of the phase transformations occurring under different conditions. The thermodynamics are already well developed, but research on the kinetics of these alloys is limited. (Barriobero-Vila et al. 2015a).

In β-alloys, which are quenched from temperatures above their β-transus, athermal ω-phase is precipitated. Within subsequent aging the ω-precipitates may undergo coarsening and serve as homogeneously distributed heterogeneous nucleation sites for the precipitating α-phase. By this ω-assisted heterogeneous nucleation a relatively large number of fine-scaled α-precipitates are formed and evenly distributed within the β-matrix. These α-precipitates often exhibit morphologies that are markedly different from precipitates nucleated from prior β-grain boundaries at higher temperatures. The mechanism describing the role of ω-precipitates in the nucleation process of α-precipitates and the influence of the ω/β-misfit determined by the alloying system is discussed in current literature and needs further development. (Dehghan-Manshadi & Dippenaar 2011; Nag et al. 2009).
This current research project endeavours to combine high-energy X-ray and neutron diffraction techniques with advanced electron microscopy techniques to explain α-phase transformation mechanisms in near-β-titanium alloys of which the Ti-1Al-8V-5Fe alloy is an example. By understanding the underlying thermodynamics and kinetics as well as related textural changes of the property determining step in the temp of these alloys, it will become possible to design new industrial processing routes for the manufacture of aerospace parts with better combinations of strength and toughness.
Theoretical Background on Titanium Alloys

2.1 Fundamental Aspects of Titanium Alloys

With a presence of about 0.6% titanium is the fourth most abundant metallic element in the earth’s crust after aluminium, iron and magnesium. Titanium has been discovered and named in 1795 by Klaproth, in the form of titanium oxide. However, it wasn’t until 1937-1940 that titanium could be produced on an industrial scale, thus enabling its use in modern technology applications. Due to its superior properties such as a very high strength to density ratio, its corrosion resistance and a considerably higher melting temperature compared to other lightweight metals such as aluminium, titanium alloys have been favoured for aerospace components such as landing gear or engine components. (Lütjering & Williams 2007, p. 2). These and other important characteristics of titanium and its alloys in comparison with other commonly used structural metallic materials are shown in Table 1.

<table>
<thead>
<tr>
<th></th>
<th>Ti</th>
<th>Fe</th>
<th>Ni</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting Temperature (°C)</td>
<td>1670</td>
<td>1538</td>
<td>1455</td>
<td>660</td>
</tr>
<tr>
<td>Allotropic Transformation (°C)</td>
<td>882: β → α</td>
<td>912: γ → α</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Crystal Structure</td>
<td>bcc → hex</td>
<td>fcc → bcc</td>
<td>fcc</td>
<td>fcc</td>
</tr>
<tr>
<td>Room Temperature E (GPa)</td>
<td>115</td>
<td>215</td>
<td>200</td>
<td>72</td>
</tr>
<tr>
<td>Approx. Level of Yield Stress (MPa)</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
<td>500</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>4.5</td>
<td>7.9</td>
<td>8.9</td>
<td>2.7</td>
</tr>
<tr>
<td>Comparative Corrosion Resistance</td>
<td>Very High</td>
<td>Low</td>
<td>Medium</td>
<td>High</td>
</tr>
<tr>
<td>Comparative Reactivity with Oxygen</td>
<td>Very High</td>
<td>Low</td>
<td>Low</td>
<td>High</td>
</tr>
</tbody>
</table>
The strong bonding with oxygen leads to a stable and adherent surface oxide layer, which guarantees the superior corrosion resistance of titanium and its alloys compared to other alloy systems up to temperatures of 873 K. Above 873 K the diffusion of oxygen through the oxide layer becomes too fast and results in excessive growth and embrittlement of the oxide layer. Disadvantages of titanium and its alloys are the generally high reactivity, its high melting point, as well as the high cost of production and manufacturing. (Lütjering & Williams 2007, p. 2,15).

Ores commonly used for the production of titanium are either rutile (TiO$_2$) or ilmenite (FeTiO$_3$). The ores are chlorinated to form a gaseous product following the chemical Reactions (1) and (2): (Lütjering & Williams 2007, p. 53-55)

\[
TiO_2 + 2Cl_2 + C \rightarrow TiCl_4 + CO_2 \quad (1)
\]

And

\[
TiO_2 + 2Cl_2 + 2C \rightarrow TiCl_4 + 2CO \quad (2)
\]

The chlorination is succeeded by a distillation step to purify the TiCl$_4$. The next stage is the Kroll process where TiCl$_4$ is reduced to form a metallic titanium sponge cake. The Kroll process follows the overall Reaction (3): (Lütjering & Williams 2007, p. 55)

\[
TiCl_4 + 2Mg \rightarrow Ti + 2MgCl_2 \quad (3)
\]

The formed sponge cake still contains some residual MgCl$_2$, thus a metallic extraction process is required. Commonly a vacuum distillation process is performed in the Kroll reactor vessel. This process is executed at temperatures of about 973-1123 K and uses the high volatility of MgCl$_2$ by evaporating it and condensing it in another vessel. The thus purified titanium sponge is now ready for the last stage in the production route –crushing and seizing. The granules won from this step have a size of about 1 to 2.5 cm depending on the end product that they are used for. (Lütjering & Williams 2007, p. 55-57).

The pie chart in Figure 1 shows the distribution of costs for the titanium sponge production subdivided into labour, maintenance, utilities and the main ingredients magnesium and TiCl$_4$. Due to the high fraction of costs associated with TiCl$_4$ in regard
to the required resources, etc. it becomes evident that the highest cost-saving potential is given here. (Lütjering & Williams 2007, p. 57).

![Pie chart of the cost distribution for the titanium sponge production.](image)

As shown in Figure 2 titanium alloys can be subdivided into α-, β- and (α+β)-alloys by the relative amount of β-phase which is retained at room temperature. The α-alloys are of hexagonal close-packed (hcp) structure and β-alloys are body-centred cubic (bcc). Due to the structural differences and also depending on the applied tmp route, the final material can have very different properties which can be tailored to suit the needs of its application. (Lütjering & Williams 2007, p. 33-36).

![Pseudo-binary phase diagram indicating the titanium alloy system classification.](image)
Theoretical Background on Titanium Alloys

The main tmp routes shall be detailed later in this chapter. At first the focus will be on a discussion of the different alloy systems of titanium and their general properties. Depending on composition, different phases will be present in the final product, which determine its properties and thus, possible applications.

2.2 Titanium Alloy Systems

Pure titanium at room temperature consists of 100% hcp \( \alpha \)-phase, at the \( \beta \)-transus temperature \( T_\beta \) of about 1155 K the structure will upon heating transform into the bcc \( \beta \)-phase. Through impurities and the addition of certain alloying elements \( T_\beta \) can be raised, lowered or completely suppressed. Therefore, depending on their effect on \( T_\beta \) impurities, or alloying elements can be subdivided into \( \alpha \)-stabilisers, \( \beta \)-stabilisers and neutral behaving elements. The classification of titanium alloys reflects on the relative amount of \( \beta \)-phase retained at room temperature. (Lütjering & Williams 2007, p. 23). Thus, near-\( \alpha \) and (\( \alpha+\beta \))-alloys have large amounts of \( \alpha \)-stabilising elements such as aluminium which leads to \( \beta \)-transus temperatures in the range 1223 to 1323 K, \( \beta \)- and near-\( \beta \)-alloys contain moderate to large amounts of \( \beta \)-stabilisers such as iron, vanadium, tungsten, molybdenum, chromium and niobium and thus \( T_\beta \) is of the order of 973 to 1123 K. (Semiatin & Furrer 2008, p. 2). The phase diagrams classifying alloying elements through their influence on the phases present in titanium are shown in Figure 3.
Figure 3: Pseudobinary phase diagrams showing the effect of alloying elements on phase transitions in titanium alloys. (Lütjering & Williams 2007, p. 24).

As most alloys of industrial importance contain both $\alpha$- and $\beta$-stabilising elements, they can be classified, as an indicator, by comparing their equivalent aluminium and molybdenum content. (Collings, Boyer & Welsch 1994, p. 10). Following Rosenberg (1970) the equivalent aluminium content for a multicomponent titanium alloy can be expressed by Equation (4), with the alloy content being inserted in wt.-%.

$$[\text{Al}]_{eq} = [\text{Al}] + \frac{[\text{Zr}]}{6} + \frac{[\text{Sn}]}{3} + 10[\text{O}]$$

(4)

In similar vein, the equivalent molybdenum content can be calculated through the content of $\beta$-stabilisers in wt.-% by Equation (5). (Collings, Boyer & Welsch 1994, p. 10; Molchanova 1965; Neelakantan, Rivera-Díaz-del-Castillo & van der Zwaag 2009).
\[
[Mo]_{eq} = [Mo] + \frac{[Ta]}{5} + \frac{[Nb]}{3.6} + \frac{[W]}{2.5} + \frac{[V]}{1.5} + 1.25[Cr] + 1.25[Ni] + 1.7[Mn] + 1.7[Co] + 2.5[Fe] - [Al]
\] (5)

Thus, the Mo-equivalent gives an indication of the \( \beta \)-stabilising ability of a multicomponent alloy.

### 2.2.1 Alpha Alloys

By convention, unalloyed titanium and multi-component alloys containing insufficient amounts of \( \beta \)-stabilisers to retain the \( \beta \)-phase at room temperature are referred to as \( \alpha \)-alloys. Since they are fully hcp, \( \alpha \)-alloys do not possess a ductile-brittle transformation temperature, a characteristic which enables their application in cryogenic devices. They are distinguished by acceptable strength and toughness levels as well as creep resistance and weldability. (Collings, Boyer & Welsch 1994, p. 6). Higher strength levels for these alloys are commonly achieved through solution strengthening with \( \alpha \)-stabilisers - in particular aluminium or the precipitation of Ti\(_3\)Al (\( \alpha_2 \)-phase).

### 2.2.2 Alpha + Beta Alloys

The (\( \alpha+\beta \))-alloys are usually alloyed with both \( \alpha \)- and \( \beta \)-stabilisers to retain a certain ratio of \( \alpha \)- and \( \beta \)-phase at operating temperatures. In general (\( \alpha+\beta \))-alloys contain 10 to 50 % of the \( \beta \)-phase at room temperature. A prominent member of this type of alloys is Ti-6Al-4V, which along with other (\( \alpha+\beta \))-alloys is distinguished by good fabricability, high room temperature strength and acceptable elevated-temperature strength. (Collings, Boyer & Welsch 1994, p. 7).

### 2.2.3 Beta Alloys

Titanium alloys containing sufficient amounts of \( \beta \)-stabilisers to retain the bcc phase upon quenching are classified as \( \beta \)-titanium alloys. In similar vein to other bcc materials \( \beta \)-titanium alloys show a ductile-to-brittle transition and are therefore unsuitable for applications at low temperature. (Collings, Boyer & Welsch 1994, p. 6-7). In contrast to \( \alpha \)- and (\( \alpha+\beta \))-alloys, \( \beta \)-alloys possess comparatively good room temperature formability. Another advantage is their ability to be hardened to high
strength levels through an ageing treatment which targets the precipitation of fine, homogeneously distributed α-particles. (Collings, Boyer & Welsch 1994, p. 31-32). The strength level can be further increased by the addition of tin and zirconium, which leads to solution strengthening of both the α- and β-phases. (Collings, Boyer & Welsch 1994, p. 32).

In the case of binary alloys, the minimum amount of β-stabiliser required to prevent the occurrence of a martensitic transformation upon quenching were determined and a few examples are listed in Table 2. (Dobromyslov & Elkin 2001).

Table 2: Amount of β-stabiliser (in at.-%) required to maintain the β-phase upon quenching. (Dobromyslov & Elkin 2001).

<table>
<thead>
<tr>
<th>Binary system</th>
<th>Ti-V</th>
<th>Ti-Cr</th>
<th>Ti-Fe</th>
<th>Ti-Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>At.-% of β-stab.</td>
<td>15</td>
<td>7</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

By comparing the Mo-equivalent (Equation (5)) of a multicomponent alloy with the value given for Mo in Table 2 it is possible to estimate the stability of the β-phase upon quenching. Hence, if the Mo-equivalent is higher than 5 at.-% the β-phase can be expected to be stabilised to room temperature when quenched from the β-transus. The martensitic start temperature $M_S$ (in K) can be estimated from the wt.-% of alloying elements by Equation (6). (Neelakantan, Rivera-Díaz-del-Castillo & van der Zwaag 2009).


(6)

### 2.3 Thermo-mechanical Processing of Titanium Alloys

The superior properties of titanium and its alloys with regard to high strength at low density, good fatigue, ductility and corrosion resistance make titanium the material of choice for use in specialty applications in the marine, aerospace or chemical industry. The application-oriented mechanical properties of titanium alloys can be achieved through microstructural modification by thermo-mechanical processing (tmp). For titanium alloys, the microstructural evolution and therefore
microstructural control depends critically on the high temperature allotropic phase transformation (from $\alpha$- to $\beta$-phase), which proceeds through a change in crystal structure from hcp to bcc. $T_\beta$, the temperature at which the $\alpha$- to $\beta$-phase transition occurs is 1155 K for pure titanium and the hot-working conditions used in the tmp routes are commonly selected relative to $T_\beta$. (Semiatin & Furrer 2008, p.1).

The processing route of titanium parts commonly follows an ingot-metallurgy approach. Large ingots are (re)melted and refined using cold-hearth or vacuum-arc techniques and then converted into mill products such as billets and sheets through the application of several tmp steps. The final components are often produced through superplastic forming or closed-die forging. Depending on the alloy classification different strategies are applied within the tmp route in order to achieve the desired microstructure and hence, mechanical properties. (Semiatin & Furrer 2008, p. 2).

### 2.3.1 Thermo-mechanical Processing of Alpha-Alloys

The tmp of $\alpha$-alloys aims at obtaining two distinctly different microstructures: equiaxed $\alpha$-phase, which can be obtained by heat treating a mechanically worked alloy below $T_\beta$ or sharp acicular $\alpha$-phase, which is achieved by water quenching from the $\beta$-phase. Structures in-between are acquired by controlling the prior $\beta$-grain size through appropriate annealing times in the $\beta$-phase field and subsequent furnace cooling. (Collings, Boyer & Welsch 1994, p. 27)

### 2.3.2 Thermo-mechanical Processing of Near-Alpha and Alpha + Beta Alloys

Since ($\alpha+\beta$)-alloys and in particular Ti-6Al-4V represent the most common type of titanium alloys, a large variety of processing techniques are used to engineer products that possess a wide range of microstructures. In general the tmp of near-$\alpha$- and ($\alpha+\beta$)-alloy ingots starts with a large amount of hot working at temperatures above the $\beta$-transus, followed by a small increment of hot working in the ($\alpha+\beta$)-phase field. This processing step is followed by a recrystallization heat treatment above $T_\beta$, which is succeeded by a secondary hot-working step in the ($\alpha+\beta$)-phase field. In the first three steps ($\beta$-hot working to $\beta$-recrystallization) the ingot structure initially
containing large columnar β-grains is transformed into a finer recrystallized β-grain structure of approximately 0.5 to 1 mm. The secondary (α+β)-hot working and annealing are employed to spherodise α-colonies, which developed during cooling following the first steps. (Semiatin & Furrer 2008, p. 2).

2.3.3 Thermo-mechanical Processing of Beta-Alloys

The use of near-β-titanium alloys in such applications as landing gear in aircraft, require an optimised combination of high strength and good ductility, in particular with respect to high fracture toughness and improved fatigue behaviour. Achievement of these properties strongly depends on the particle size and homogeneity of the α-phase precipitate distribution in the β-matrix. (Lütjering & Williams 2007, p. 36). The α-phase nucleates preferably at β-grain boundaries to form a continuous α-layer, but this continuous layer of α-phase shows a deleterious effect on mechanical properties. One of the main goals of tmp is to reduce the formation of a continuous layer of α-phase on the grain boundaries. There are two major options of creating improved nucleation conditions for α-phase precipitation. The first option is to cold work before ageing, a treatment that increases the number of dislocations. Alternatively, a two-step ageing treatment involving precipitation of intermediate ω- or β'-phase can be used. Both methods will increase the number of α-nucleation sites within the β-matrix and thus reduce the thickness of the α-layer that forms on β-grain boundaries. (Lütjering & Williams 2007, p. 41-42).

2.4 Phases in Titanium Alloys

Depending on composition and the tmp route a variety of phases can be present in titanium alloys. Some phases such as the ω-phase are in general metastable and would transform into a different phase, usually α-phase, upon heat treating. (Collings, Boyer & Welsch 1994, p. 24). The phases pertinent to this study are listed with their crystallographic data in Table 3. The metastable ω- and α”-phase can possess different atomic positions depending on their stability and the respective moment during the phase transformations. These alterations in atomic positions are expressed through a z-value in the case of ω-phase and a y-value for α”-phase. The ideal ω-phase is of hexagonal structure with a z-value of zero, the trigonal case is for
Theoretical Background on Titanium Alloys

0 < z < 1.67 and in a hexagonal arrangement of the bcc unit cell z equals 0.167 which reflects on the formation mechanism of the ω-phase as will be detailed in Section 2.5. (Sikka, Vohra & Chidambaram 1982, p. 256). The α”-phase can be understood as a transitional phase between β- and α-phase. (Duerig et al. 1982). This reflects on the atomic positions as y can be 1/6 < y < 1/4 with y close to 1/6 indicating the structural proximity to the α-phase and y close to 1/4 indicating the structural proximity of α”- to the β-phase. (Obbard et al. 2011).

Table 3: Crystallographic data of phases in titanium pertinent to this study (Duerig et al. 1982; Hull 1921; Levinger 1953; Lütjering & Williams 2007, p. 16; Obbard et al. 2011; Sikka, Vohra & Chidambaram 1982, p. 254-256)

<table>
<thead>
<tr>
<th>Phase</th>
<th>Space Group</th>
<th>Structure</th>
<th>Lattice Parameters / Å</th>
<th>Atomic Coordinates (XYZ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Ti</td>
<td>P6/ mmc</td>
<td>Hcp</td>
<td>a=2.95 c=4.68 c/a=1.587</td>
<td>0 1/3 0 1/2</td>
</tr>
<tr>
<td>β-Ti</td>
<td>Im3m</td>
<td>Bcc</td>
<td>a=3.32</td>
<td>0 1/2 0 1/2</td>
</tr>
<tr>
<td>ω-Ti</td>
<td>P6/mmm</td>
<td>Hexagonal</td>
<td>a=4.625 c=2.813 c/a=0.608</td>
<td>0 2/3 1/3 1/2 + z</td>
</tr>
<tr>
<td>α”-Ti</td>
<td>Cmcm</td>
<td>Orthorombic</td>
<td>a=3.01 b=4.91 c=4.63</td>
<td>0 0 0.5 0.5 1/4 3/4 1/4 3/4</td>
</tr>
</tbody>
</table>
2.4.1 Systematics of Phase Stability

When assessing the influence of alloying elements or external factors on phase stability in titanium alloys some universal considerations regarding fundamental differences of the bcc and the hcp structures should be taken into consideration. Dissimilarities resulting from the differences in the crystal and also electronic structures will constitute to the effects of the prevailing conditions such as alloy composition or temperature on phase stability.

Variations in packing density will affect the stability range for the phases in regard to temperature and also affect the solubilities of alloying elements due to atomic size considerations. The bcc lattice with a 68% packing density is relatively more open as compared to the hcp lattice which possesses a packing density of 74%. As a result the bcc structure retains higher vibrational entropy than the alternative structure. Thus, while increasing the temperature the free energy of a bcc lattice decreases faster than the free energy of the other two lattices. Consequently, during heating of pure titanium the hcp α-phase which is more stable at lower temperatures will transform into the bcc β-phase. Therefore, atomic size effects of alloying elements have to be taken into account when considering their influence on phase stabilities. (Collings, Boyer & Welsch 1994, p. 5).

Electronic cohesive forces are another more dominant phase stabilising mechanism. (Collings, Boyer & Welsch 1994, p. 5-6). A correlation exists between crystal structure and the electron/atom ratio which describes the “electron concentration” after atomic volume correction. Thus, electronic structure plays an important role in regard to phase stability. (Collings, Boyer & Welsch 1994, p. 5-6). Collings, Ho and Jaffee (1973) showed that when comparing a pair of allotropes the more stable one shows a lower electronic density of states on the Fermi level which was exemplified by data for α- and β-phase and β- and ω-phase. In that regard it is interesting to note that most α-stabilisers and neutral behaving elements are either simple metals or interstitial elements whereas β-stabilisers are in general transition metals and thus possess unfilled or just-filled d-electron bands. When simple metals such as aluminium are in solid solution in titanium most electrons will accommodate states at the lower part of the band and only very few will appear on the Fermi level.
Aluminium atoms are avoided by titanium d-electrons thus reducing the electron density between Ti-Al. Consequently, pre-existing Ti-Ti bond directionality is emphasised and the hcp structure is preserved. On the contrary, adding transition metals with an electron/atom ratio higher than 4.1 increases the electron density and thus stabilises the bcc structure. (Collings, Boyer & Welsch 1994, p. 6-7). Ageev and Petrova (1970) found that β-stabilisers which are transition metals are more effective the further they are to the right of titanium in the periodic table of elements since that means that their electron/atom ratio increases. They also state that an addition of a β-stabiliser needs to result in an electron/atom ratio of at least 4.2 in order to be able to retain the metastable β-phase upon quenching.

2.4.2 Equilibrium Phases

When the bcc β-phase transforms into the hcp α-phase, the crystallographic orientation relationship follows the Burgers relationship shown in Equation (7).

\[
\{110\}_\beta || \{0001\}_\alpha \\
\langle 111 \rangle_\beta || \langle 11\overline{2}0 \rangle_\alpha
\] (7)

Consequently the resulting α-phase can exist in 12 variants showing different orientations with respect to the parent β-structure. (Lütjering & Williams 2007, p. 29).

2.4.3 Nonequilibrium Phases

2.4.3.1 Martensite

If pure titanium or relatively solute lean titanium-transition metal alloys are quenched from the β-phase, the resulting phase is the hcp martensitic structure α’. (Collings, Boyer & Welsch 1994, p. 38). Following Otte (1970) the β- to α’-phase transformation can be described by the activation of the shear systems shown in Equation (8).

\[
[111]_\beta (1\overline{1}2)_\beta \equiv [2\overline{1}13]_\alpha’ (\overline{2}112)_\alpha’
\] (8)
\[ [111]_{\beta} (\bar{1}01)_{\beta} \equiv [2\bar{1}3]_{\alpha'} (\bar{1}011)_{\alpha'} \]

The \( \alpha' \)-transformation can be characterised through a habit plane close to \{334\}_{\beta} and also follows the Burgers relationship given in Equation (7). (Davis, Flower & West 1979b; Shibata & Ono 1977; Williams 1973). Davis, Flower and West (1979b) studied the Ti-Mo system and discovered that the martensitic transformation to \( \alpha' \)-phase is achieved through a contraction of 10% along \[100\]_{\beta}, an expansion of 10% along \[01\bar{1}\]_{\beta} and an expansion of 1% along \[011\]_{\beta} which corresponds to \[2\bar{1}10\]_{\alpha'}, \[01\bar{1}0\]_{\alpha'} and \[0001\]_{\alpha'} respectively.

Another martensitic phase, \( \alpha'' \) of orthorhombic structure can be found under mainly two conditions. Firstly, in titanium alloys that contain transition metals where the solute content exceeds certain limits, the martensitic transformation will lead to the formation of \( \alpha'' \)-phase. Secondly, Williams (1973) found that martensite which is not formed upon quenching but stress-induced, is always of the orthorhombic variety. By studying Ti-20 at.-% Nb, Hatt and Rivlin (1968) found the \( \beta \)- to \( \alpha'' \)-phase orientation relationship shown in Equation (9) with an accuracy of \( \pm 0.5^\circ \). The geometric relations between \( \beta \)- and \( \alpha'' \)-phase and \( \alpha \)- and \( \alpha'' \)-phase are shown in Figure 4.

\[\begin{align*}
\langle 100 \rangle_{\alpha'} & \ 2^\circ \ from \ \langle 100 \rangle_{\beta} \\
\langle 010 \rangle_{\alpha'} & \ 2^\circ \ from \ \langle 110 \rangle_{\beta} \\
\langle 001 \rangle_{\alpha'} & \ \parallel \ \langle 1\bar{1}0 \rangle_{\beta}
\end{align*}\] (9)

Figure 4: Orthorhombic setup of the bcc (left) and hcp (right) structures. (Duerig et al. 1982).
2.4.3.2 Omega Phase

In many β-titanium alloys where the martensitic reaction is suppressed by the presence of alloying elements, the β-phase decomposes upon quenching into athermal ω phase. In alloys with a high content of β-stabilisers ω phase is of trigonal symmetry and of hexagonal symmetry in the case of leaner alloys. Figure 5 shows the necessary changes that the bcc crystal has to undergo to complete the transformation into the ω-phase. Further information of the β- to ω-phase transformation mechanism is given in Section 2.5.

Figure 5: Required structural changes to form ω-phase from β-phase, also showing the incomplete transition to a trigonal ω-structure. (Stark 2009, p. 8).

The ω-phase can also appear as a transitional phase before the α-phase is precipitated at intermediate heating temperatures or slow heating rates following quenching from above Tβ, in which case it is referred to as isothermal ωiso-phase. Isothermal ωiso-phase possesses the same crystallographic symmetry as athermal ω phase, but is more solute lean with respect to the surrounding β-matrix. (Lütjering & Williams 2007, p. 30-31). The orientation relationships between α-, β- and ω-phases are given by Equation (10).

\[
\begin{align*}
\{0001\}_\alpha & \parallel \{1\bar{1}0\}_\beta \parallel \{1\bar{1}20\}_\omega \\
\langle 1\bar{1}20\rangle_\alpha & \parallel \langle 111\rangle_\beta \parallel \langle 0001\rangle_\omega
\end{align*}
\] (10)

With four sets of <111>β directions, four possible crystallographic variants result for the ω-structure from a given bcc parent crystal. Figure 6 shows the reflections for the four ω-variants viewed from the [113]β zone axis. (de Fontaine, Paton & Williams 2019, p. 30-31).
Figure 7 depicts the [101̅]_β zone axis with additional reflections for ω₁ (contributing to 1/3<121>β and 2/3<121>β reflections) and ω₂ (contributing to 2/3<111>β and 1/3<141>β reflections). (Sukedai, Hashimoto & Tomita 1991).

2.5 Mechanism of the Beta to Omega Phase Transformation

Conditions enabling metastable ω-precipitation are a suitable alloy composition to form ω-phase upon quenching or subsequent heating with suitable heating parameters. The ω-phase can also form through quenching to very low temperatures. By applying very high hydrostatic pressures the ω-phase can be stabilised. (Sikka, Vohra & Chidambaram 1982, p. 250-252). The β- to ω-phase transformation can be achieved through a displacement of atomic layers of ±1/12 along [111]_β or ±1/6 along [0001]_β (for a hexagonal arrangement of the bcc lattice) respectively as shown in Figure 5. In terms of the lattice parameters the atomic displacement can be
expressed as $\pm \frac{\sqrt{3}}{12} a_\beta$ and $\pm \frac{1}{6} c_\omega$ respectively. The resulting correlation between the lattice parameters of $\beta$- and $\omega$-phase is given in Equation (11). Thus, an atomic displacement $<\frac{\sqrt{3}}{12} a_\beta$ will result in a trigonal arrangement of the $\omega$-phase. (Sikka, Vohra & Chidambaram 1982, p. 257). The atomic displacement for forming the hexagonal $\omega$-phase can also be described as merging two former $(222)_\beta$ to form a new plane following the pattern $...-A-B-C-A-B-C-...$ to $...-A-(BC)-A-(BC)-...$. This plane collapse is assumed to work in two steps involving an intermediate trigonal phase. (Lütjering & Williams 2007, p. 31).

$$a_\omega = \sqrt{2} a_\beta$$

$$c_\omega = \frac{\sqrt{3}}{2} a_\beta$$

As a group IV transition metal, titanium possesses a natural dip within the bcc-lattice phonon spectrum at $\frac{2}{3} <111>_\beta$. (Stassis, Zarestky & Wakabayashi 1978). This dip seems to be the origin of the $\omega$-phase formation and builds the foundation of the linear fault model which aims to explain the existence of $\omega$-phase and also to demonstrate the required changes in the crystal structure to go from $\beta$- to $\omega$-phase. (de Fontaine 1970; Myron, Freeman & Moss 1975). The linear fault model explains that due to the dip in the $<111>_\beta$ direction neighbouring atoms at temperatures above the beta transus tend to arrange themselves in a form of short-range order which can be understood as a line defect in the $<111>_\beta$ direction. These deviations from the expected local atomic arrangement are independent from each other at these temperatures so that no long-range ordering can be observed. Thus, in near-$\beta$-titanium alloys at elevated temperatures uncorrelated line defects are present in the $<111>_\beta$ direction. These defects are the origin of a localised $\{111\}_\beta$ plane collapse which can be understood as embryonic $\omega$-phase. When cooled to temperatures closer to $\omega_{iso}$-formation the defects are correlating and discrete $\omega$-particles precipitated. (Banerjee, Tewari & Dey 2006). The linear fault model explaining $\omega$-formation and the required atomic movements in the bcc crystal to form the $\omega$-phase are shown in Figure 8.
The necessary transverse sinusoidal displacement wave of amplitude $\frac{1}{3} <112>_{\beta}$ is equivalent to the longitudinal sinusoidal phonon displacement wave of $\frac{2}{3} <111>_{\beta}$ as described by de Fontaine, Paton and Williams (1971). This displacement wave of ω-formation is depicted in Figure 9. Thus, for a complete β- to ω-phase transformation, the planes on positions ‘0’ and ‘1’ would maintain its position whereas the planes on ‘$\frac{1}{3}$’ and ‘$\frac{2}{3}$’ would reposition to the intermediary ‘$\frac{1}{2}$’ position. (de Fontaine, Paton & Williams 1971).

Figure 9: The required sinusoidal displacement wave to form ω-phase from bcc stacking. (de Fontaine, Paton & Williams 1971).
Resulting from this displacement wave, the stacking sequence of \((222)_\beta\) planes needs to change from \(\ldots-A-B-C-A-B-C-\ldots\) to \(\ldots-A-B'-A-B'-\ldots\). Thus, A planes remain unchanged but B’ planes exhibit a trigonal arrangement of nearest neighbour atoms. Figure 10 shows that depending on the level of completion to which the displacement wave is followed, the resulting \(\omega\)-phase will either be of trigonal or hexagonal symmetry. (de Fontaine, Paton & Williams 1971).

![Figure 10](image)

Figure 10: Depending on the extent to which \((222)\) planes in the bcc lattice follow the displacement wave, the resulting \(\omega\)-phase will be trigonal (incomplete) or hexagonal (complete). (Lütjering & Williams 2007, p. 31).

The models outlined above lead to the conclusion that in general, the \(\beta\)- to \(\omega\)-phase transformation shows characteristics of both a diffusional and a displacive type of phase transformation. By studying a Ti-18% Mo alloy Nag et al. (2011) found that the \(\beta\)- to \(\omega\)-phase transformation follows a novel mixed-mode type of first order transition in which diffusion and displacement occur coupled yet continuously. In the as-quenched alloy compositional fluctuations lead to structural instabilities of Mo-depleted regions resulting in a local collapse of \(\{222\}_\beta\)-planes which can be understood as \(\omega\)-like embryos. Given the applied temperature is sufficient to allow for diffusion, Mo will be rejected from those embryos into the \(\beta\)-matrix and thereby the precipitates develop a fully hexagonal structure. (Nag et al. 2011).
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The transformation from the bcc β-phase to the hcp α-phase in titanium alloys would in general either occur martensitically or through diffusion controlled nucleation and growth, depending on the prevailing conditions such as cooling rate or alloy composition. (Lütjering & Williams 2007, p. 29) For β-titanium alloys with a sufficient amount of alloying elements, the alloy can decompose upon quenching or subsequent heat treatment possibly involving non-equilibrium phases such as the ω-phase as indicated in Figure 11. (Lütjering & Williams 2007, p. 30).

Figure 11: Pseudo-binary phase diagram including non-equilibrium phases resulting from selected heat treatment conditions. (Lütjering & Williams 2007, p. 39).

3.1 Research on Phase Transformations in Binary Titanium Alloys

In order to develop theories of the mechanism and rate of phase transformations in complex systems such as near-β-titanium alloys, it is useful to start with simpler systems such as binary alloys. The following sections present findings on the interrelation of heat treatment parameters and composition and their combined effects on phase transformations in binary near-β-titanium alloys.
3.1.1 Interrelation of Composition and Cooling Rate and Their Influence on the Mechanism of Beta Phase Transformation

When near-α- and (α+β)-alloys are quenched from above their transus temperature $T_\beta$ they will form a martensitic structure. However, if the cooling rate is low enough to allow for α-nucleation and growth, a Widmanstaetten structure is formed instead. Collings, Boyer and Welsch (1994, p. 34-36) state that by increasing the alloying content of binary transition metal alloys the martensitic start temperature, $M_s$, is lowered so that the martensitic transformation to $\alpha'$- or $\alpha''$-phase is not completed. Depending on the type and amount of alloying elements $\omega_a$-phase is formed in addition. A consequence of the lower free energy of martensite as compared to $\omega$-titanium is that $\omega$-precipitates are consumed by growing martensite needles. As depicted in Figure 12, the overlapping (α+ωₐ+β)-region is rather narrow and depends on the electron/atom ratio of the titanium alloy. By further increasing the content of β-stabilisers, $M_s$ can be reduced before a martensitic transformation is suppressed when quenching to room temperature and only $\omega_a$-phase is formed in the retained β-matrix. In a subsequent heat treatment at relatively low temperatures, of about 573 K, $\omega_{iso}$-phase will be precipitated. (Collings, Boyer & Welsch 1994, p. 34).
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Figure 12: Influence of electron/atom ratio on phase occurrence in titanium alloys upon quenching and subsequent heat treatment at intermediate temperatures. (Collings, Boyer & Welsch 1994, p. 34).

By increasing the α-stabiliser content of a titanium alloy, the martensitic start temperature $M_s$ increases whereas it decreases with increasing β-stabiliser content (Collings, Boyer & Welsch 1994, p. 38). Figure 13 shows the influence of various alloying elements on $M_s$. Upon cooling there will be a competition between the classic nucleation and growth type of phase transformation, which depends on the availability of thermally activated diffusion, and the martensitic type of transformation that is in the ideal case, completely independent of thermal activation and would take place at high, temperature-independent rates. In general, most transformation processes cannot strictly be identified as being only one of these mechanisms since they might contain characteristics of both, especially because alloying element additions will influence the degree to which one or the other of these mechanisms will be favoured. (Collings, Boyer & Welsch 1994, p. 36).

![Figure 13: Influence of alloying content (in weight-% of various elements) on the martensitic start temperature. (Zwicker 1974, p. 174).](image)

When comparing different elements and their respective influence on $M_s$, it is important to maintain a constant cooling rate. Jepson, Brown and Gray (1970) were able to show for Ti-5% Nb (at.-%) that the $M_s$-temperature is a function of the quench rate. When the cooling rate was increased from $10^{-3}$ K/s to 10 K/s the martensitic
start temperature was lowered from 983 K to 933 K. They also showed that after the critical quench rate of 32 K/s was reached, $M_s$ became independent of the quench rate in a Ti-5\% Nb alloy. By increasing the niobium content from zero to 15 at.-\%, they were able to show that the critical quench rate is dependent on composition and decreased from 200 K/s to $\sim$0.4 K/s with increasing niobium content. (Jepson, Brown & Gray 1970). As can be seen in Figure 13 increasing the niobium alloying content lowers the martensitic start temperature of the alloy which can lead to an incomplete transition. However, at the same time niobium also lowers the critical quench rate which leads to $M_s$ being more independent of the quench rate. (Jepson, Brown & Gray 1970). Dependencies of both $M_s$ and the critical quench rate on the alloy composition can be explained through the simultaneous necessity of the system to adopt a structural transformation whilst maintaining compositional homogeneity. (Collings, Boyer & Welsch 1994, p. 35-36). Thus, an increase in certain alloying elements leads towards a decreased favourability of the martensitic transformation to occur due to energy considerations between enforcing a spontaneously occurring change in structure and maintaining a metastable $\beta$-phase.

3.1.2 Influence of Composition and Alloying Element Diffusivities on the Beta Phase Transformation Mechanisms

Through their effects on lattice parameters or the interaction with dislocations alloying elements have long- and short-range effects on the crystal lattice which influence the transformation behaviour of the alloy and thus the resulting microstructure. (Collings, Boyer & Welsch 1994, p.36). A long-range effect through alloying is given through the influence on the lattice parameters. (Collings, Boyer & Welsch 1994, p.36). Also, alloying elements can have a short-range effect on the local crystal lattice through interactions with dislocations and other lattice faults. These interactions may lead to a localised suppression of atomic plane movement and thus, limit the cooperative distance of atomic regions. (Collings, Boyer & Welsch 1994, p. 36). Furthermore, a short-range effect resulting from alloying is the influence on transformation kinetics. By influencing the critical quench rate that is required to induce a martensitic transformation mechanism the solute content under otherwise constant cooling conditions will determine the resulting transformation structure.
An example for the influence of an alloying element on transformation mechanisms can be seen in Mo. It has been shown by Devaraj et al. (2012) on a Ti-Mo alloy that fully developed ω-phase can only be found in regions depleted in Mo. Thus, indicating that Mo hinders the necessary \{111\}_β plane movement and therefore ω-precipitation.

The influence of alloying elements on lattice parameters can be summarised as follows. The lattice constants at room temperature for α-phase in the case of pure titanium were determined as $a \approx 2.95 \text{ Å}$ and $c \approx 4.68 \text{ Å}$ leading to a $c/a$ ratio of $\sim 1.585$ which is smaller than close-packed $c/a$ ratio of 1.633. As impurities such as interstitial alloying elements mostly effect $c$, leading to its increase, the lowest value was chosen to be most likely correct. (Zwicker 1974, p. 64). Alloying with aluminium leads to a continuous decrease of $a$ with increasing Al-content. However, $c$ was found to remain almost constant up to Al-contents of approximately 3 at.-% and slightly decrease for higher contents. Thus, alloying with aluminium leads to an increase in $c/a$. (Zwicker 1974, p. 66-67). The ω-lattice parameters were determined under a pressure of 85 kbar as $a \approx 4.63 \text{ Å}$ and $c \approx 2.81 \text{ Å}$. (Zwicker 1974, p. 65). The lattice parameter for β-titanium was estimated to be $a \approx 3.275 \text{ Å}$ under standard conditions. (Dobromyslov & Elkin 2001). Most substitutional alloying elements of the β-stabilising type will decrease the β-lattice parameter. Figure 14 shows the influence of the atomic concentration of d-metals of the 4th period on the β-lattice parameter. (Dobromyslov & Elkin 2001).
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Figure 14: Change of β-lattice parameter with alloying content of d-metals of the 4th period. (Dobromyslov & Elkin 2001).

Collings, Boyer and Welsch (1994, p. 35-36) found that the diffusion coefficient of the respective solute in the β-phase, determines the extent to which either of the two competing mechanisms, nucleation and growth or martensitic transformation, dominates. Binary titanium alloys containing transition metals with a group number equal to or smaller than (V) such as vanadium or niobium can in general be water-quenched without decomposition of the β-phase. However, this is not necessarily true for alloys containing transition metals with group numbers higher or equal to (VIII) such as iron or cobalt. These differences in required quenching conditions originate from the different diffusion coefficients of elements in the β-phase. (Collings, Boyer & Welsch 1994, p. 35-36). Figure 15 shows the diffusion coefficient for various β-stabilisers in the β-phase at 1273 K. It can be seen that a general trend exists for an increase of the diffusion coefficient with the group number. For example, the diffusion coefficient of iron is \~60 times higher than that of molybdenum. Thus, transition element alloys with higher group numbers such as Fe, can contribute to a diffusion driven phase transformation more easily and consequently require higher quench rates to avoid β-phase decomposition. (Collings, Boyer & Welsch 1994, p. 35-36).
The diffusivity of alloying elements has a strong influence on the solution and ageing heat treatments and also the recrystallisation and hot working temperatures of titanium. Therefore, it is instructive to assess both the substitutional and interstitial diffusion rates of various elements in the α- and β-titanium phases as compared to the self-diffusion rate of Ti. (Lütjering & Williams 2007, p. 45). Figure 16 shows the diffusivities of different elements in the β- and α-phases of titanium and it follows that it is not only interstitial elements that can have higher diffusion rates than the self-diffusion rate of titanium, but substitutional alloying elements can diffuse faster as well.

Fe and O are part of the group of elements which exhibit higher diffusivities in β-titanium than the self-diffusivity. Ni, Cr and Mn possess diffusivities of a similar order of magnitude. (Lütjering & Williams 2007, p. 45; Mishin & Herzig 2000). However, some elements have lower diffusivity rates in β-titanium as compared to the self-diffusivity of titanium. Examples for this type of alloying elements are Al and Mo as shown in Figure 16 and V, Sn and Nb also lie in a similar range. (Lütjering & Williams 2007, p. 45; Mishin & Herzig 2000).
State of Research on Phase Transformations in Near-Beta Titanium Alloys

Figure 16: Arrhenius plot of element diffusivities in α- and β-titanium. (Liu & Welsch 1988; Lütjering & Williams 2007, p. 46; Mishin & Herzig 2000; Zwicker 1974, p. 102-113).

In α-titanium Fe, Ni and Co show exceptionally high diffusion rates which is due to an interstitial diffusion mechanism that also affects the vacancy diffusion rate in α-titanium and thus the self-diffusivity and Al diffusion rates. (Lütjering & Williams 2007, p. 45; Mishin & Herzig 2000). As a result the rate of diffusion of substitutional elements in α-titanium strongly depends on the level of Fe impurity or the alloying content of Fe, Ni and Co respectively. (Lütjering & Williams 2007, p. 45; Mishin & Herzig 2000). Mn and Cr are also part of the group of elements with diffusion
coefficients higher than the self-diffusion coefficient of Ti although their diffusion rates are about two orders of magnitude lower than those of Fe, Ni and Co. (Lütjering & Williams 2007, p. 45-46; Mishin & Herzig 2000). Elements diffusing through the normal vacancy mechanism with diffusivities close to Al are Zr, Hf, Au, In and Ga. (Lütjering & Williams 2007, p. 45; Mishin & Herzig 2000). Thus, the type of alloying element is of major significance when assessing the sequence and kinetics of a phase transformation. Hence, an alloying system based on Ti-Fe should display significantly different behaviour than one based on Ti-Mo.

3.1.3 Resulting Microstructures of Beta Phase Transformation and Their Dependence on Type and Amount of Alloying Elements

The type and amount of solute will determine at a given quench rate, the extent to which the pertaining phase transformation is athermal or alternatively, shear or diffusion driven nucleation and growth. (Collings, Boyer & Welsch 1994, p.36). Thus, the resulting microstructure for a relatively solute-lean alloy would resemble massive martensite (also called lath or packet martensite) in this case the structural change occurs on a large scale with considerable coherence. This massive martensite is built up of 50 to 100 μm large zones, which consist of parallel arranged fine platelets with a thickness of about 1 μm. (Collings, Boyer & Welsch 1994, p.36). With an increase in alloy content the coherence of the colonies is lost and the structure changes towards acicular martensite in which individual platelets are disordered. (Collings, Boyer & Welsch 1994, p.37). By further increasing the solute content a complete transformation is prevented and the β-phase is retained between the acicular martensite platelets. This retained-β plus acicular martensite structure resembles a Widmanstaëtten arrangement in which the long axes of the α-needle lies parallel to (110)_β planes. (Collings, Boyer & Welsch 1994, p.37).

Studies on the Ti-Mo system by Bagariatskii, Nosova and Tagunova (1958), Davis, Flower and West (1979b) Flower, Davis and West (1982) describe the change in resulting microstructure after the phase transformation due to solute content: Ti-2 wt.-% Mo transforms almost completely to acicular martensite upon quenching and only a small amount of massive martensite will be formed. By further increasing the molybdenum content to 4 wt.-% or more, the morphology will be fully acicular.
Above 4 wt.-% Mo the martensite type changes from α’- to α”-phase. Retained β-phase was found in Ti-2 wt.-% Mo and Ti-4 wt.-% Mo but could not be detected in Ti-6 wt.-% Mo and Ti-8 wt.-% Mo. Collings, Boyer and Welsch (1994, p.39) conclude from these findings that in titanium alloys containing moderate amounts of transition metals, the high $M_s$ temperature requires very high quench rates to completely suppress diffusion of the β-stabilisers. If the quench rates are not high enough molybdenum can segregate and stabilise some of the β-phase to room temperature. By further increasing the β-stabiliser content, $M_s$ is lowered to a temperature range in which moderate quench rates are sufficient to suppress diffusion and a fully martensitic transformation takes place. If the β-stabiliser content is increased further so that $M_f$ lies below room temperature, some β-phase will be retained regardless of the cooling rate. (Collings, Boyer & Welsch 1994, p.39). Another observation worth highlighting from this study is that as the β-phase increases in stability due to an increasing β-stabiliser content, the martensite that forms upon quenching will be α”- and not α’-phase. This was explained by Duerig et al. (1982) through a reduction of the magnitude of required lattice strains upon formation of β- to α”-phase as compared to β- to α’-phase. So that α”-phase can be understood to be a transitional phase before equilibrium α-phase would form during a subsequent heat treatment (if applied). Finally it should be noted that the sequence of transformation and thus the resulting microstructure in a given heat treatment is strongly dependent on the alloying element diffusivities. It was shown in Section 3.1.2 that the diffusivity of Mo in both the β- and α-phases is very low so that findings relevant to Ti-Mo alloys cannot be unconditionally applied to alloys based on elements that diffuse faster than Mo, such as Fe.

It was argued in Section 3.1.1 that titanium alloys with a sufficiently high β-stabiliser content can form ω$_a$-phase upon quenching and the ω$_{iso}$-phase can precipitate upon holding at intermediate temperatures. In binary titanium alloys the misfit between ω-precipitates and the β-matrix is the determining factor with respect to ω-precipitate morphology as well as the temperature range in which the ω-phase can be maintained. (Williams, Hickman & Leslie 1971). The misfit between matrix and precipitate depends on the type and amount of binary alloying elements. For misfits
smaller than 0.5 %, ellipsoidal particles form and misfits greater than 0.5 % result in the formation of cubical \( \omega \)-particles. (Williams, Hickman & Leslie 1971). An example for a low-misfit system with ellipsoidal precipitates would be Ti-Mo, whereas a typical high-misfit system with cubical shaped precipitates would be the Ti-Fe system. Examples of dark field images showing \( \omega \)-morphologies in a Ti-Mo alloy and a Ti-Fe alloy are shown in Figure 17. Thus, the morphology is a result of energy minimisation. For high-misfit systems the driving force originates in minimisation of strain energy whereas surface energy minimisation is predominant in low-misfit systems. (Duerig, Terlinde & Williams 1980).

![Dark field images showing \( \omega \)-morphologies](image)

Figure 17: Dark field images of a \( \{10\bar{1}1\}_\omega \) reflection showing left: Ellipsoidal \( \omega \)-particles aligned along \( <111>_{\beta} \) in Ti-11.6Mo; right: Cubical \( \omega \)-particles aligned along \( <100>_{\beta} \) in Ti-10Fe. (Williams & Blackburn 1969).

Williams, Hickman and Leslie (1971) argue that the misfit between matrix and precipitates in binary titanium alloys influences the temperature range in which \( \omega \)-phase exists. In lower misfit systems the stability of the \( \omega \)-phase is increased so that it will be present up to higher temperatures and for longer holding times as compared to high-misfit systems. However, this correlation does not seem to hold for multicomponent titanium alloys. (Williams, Hickman & Leslie 1971).

### 3.2 State of Research on Phase Transformations in Multicomponent Near-Beta Titanium Alloys

Much research on phase transformations in binary titanium alloys relevant to the present study has been done and theories aimed at predicting phase stabilities and the resulting microstructures have been briefly referred to in Section 3.1. Most
titanium alloys of industrial significance are multicomponent systems, but assessments of binary titanium alloys can provide a platform for the better understanding of the pertaining mechanisms of the phase transformations occurring in multi-component systems. Therefore, studies on ternary systems and eventually real multi-component alloys are necessary to extend the findings based on binary systems and to develop new approaches to assess multicomponent alloys.

3.2.1 Influence of Ternary Additions on the Beta Phase Transformation in Metastable Beta Titanium Alloys

Williams, Hickman and Leslie (1971) investigated the influence of the addition of a third element to Ti-Mo and Ti-V binary alloys. They added the α-stabilisers Al and O and the relatively neutral behaving elements Sn and Zr. In their study samples of each composition have been solution treated above $T_{\beta}$, quenched to room temperature and then subjected to a variety of subsequent heat treatments in which α- and ω-phases precipitated. Williams, Hickman and Leslie (1971) found that all additions lowered the amount of ω-phase formed during heat treatment, reduced the upper temperature limit of ω-phase formation and also the duration at which ω-phase can exist in Ti-V and Ti-Mo alloys before the α-phase is precipitated. These results are summarised on the example of aluminium additions to Ti-V in Figure 18.
The study also revealed that the influence of the misfit between the β-matrix and ω-precipitates on the resulting morphology of ω-precipitates is the same in ternary and binary alloys investigated. Thus, a lattice misfit < 0.5 % results in an ellipsoidal ω-morphology whereas a misfit > 0.5 % generates cubical ω-precipitates. (Williams, Hickman & Leslie 1971).

However, findings from binary alloys with respect to the interrelation of ω-phase stability and lattice misfit of the precipitate cannot be transferred to ternary alloys. In ternary alloys misfit is not the only determining factor with respect to ω-phase stability. Because the investigated additives decreased the stability range of the ω-phase, but affected the β-lattice parameter and thus the lattice misfit between precipitate and matrix in opposing ways. (Williams, Hickman & Leslie 1971). Figure 19 shows that the additions of Sn, Zr and O to Ti-V and Ti-Mo alloys increase the β-
lattice parameter and hence decrease the misfit whereas Al reduces the β-lattice parameter, which would increase the misfit. Thus, concluding from the misfit alone only Al should limit the ω-phase stability, which highlights the fact that other factors promoting nucleation and growth of the α-phase are more important in multicomponent alloys than the in- or decrease of misfit. (Williams, Hickman & Leslie 1971).

![Figure 19: β-Lattice parameter variations in Ti-6Mo, Ti-20V and Ti-25V due to ternary element additions. (Williams, Hickman & Leslie 1971).](image)

Williams, Hickman and Leslie (1971) observed that alloys which did not precipitate the ω-phase upon quenching or within subsequent heat treatments in detectable amounts, developed small homogeneously distributed precipitates instead. These precipitates were accompanied by pronounced reciprocal lattice streaking, but showed no new discrete reflections in selected area electron diffraction patterns of thin foils during transmission electron diffraction studies. X-ray diffraction patterns taken from these samples showed peak broadening of high angle bcc peaks. When continuing the ageing process, α-phase nuclei were found within those precipitates. Williams, Hickman and Leslie (1971) found that these precipitates should be a form of solute-lean β-phase (subsequently referred to as β’), which would explain why the α-phase preferably nucleates within this region (given that it minimises
compositional fluctuations). The proposed resulting pseudo-binary phase diagram which incorporates the solute lean β’ phase is shown in Figure 11. (Williams, Hickman & Leslie 1971). As will be detailed in the following section, other studies confirmed a tendency towards spinodal decomposition in certain near-β-titanium alloys. In particular, alloys containing Mo and Cu appear to show this effect.

3.2.2 Influence of an Intermediate Phase Transition on Alpha Phase Nucleation and Growth in Multicomponent Near-Beta Titanium Alloys

Most near-β-titanium alloys contain at least two different β-stabilisers and at least one α-stabiliser, usually Al. Therefore, the study of Williams, Hickman and Leslie (1971), which only considered the amount of α-stabilisers neutral behaving elements cannot fully predict the final microstructures and thus properties of β-titanium alloys following the tmp. Therefore, recent research focused on multicomponent near-β-alloys such as Ti-10V-2Fe-3Al or Ti-5Al-5Mo-5V-3Cr in an attempt to determine the influence of an intermediate β’-, ω- and α”-phase transformation on the final precipitation of the α-phase.

While investigating the influence of cooling rate on the ω-phase transformation mechanism in Ti-10V-6Cu Ng et al. (2011) found a link between solute lean β’-regions formed through spinodal decomposition during air-cooling from above T_β and subsequent ω-precipitation. Here, ω-phase was formed preferentially in β’-regions with a cuboidal morphology whereas water quenching from above T_β followed by a 60 second anneal at 773 K led to ellipsoidal ω-precipitates showing only minor compositional fluctuations, which were similar to the fluctuations observed in the β-matrix. However, Duerig, Terlinde and Williams (1980) were able to show for a Ti-10V-2Fe-3Al alloy, that ω-particles which were initially of an ellipsoidal shape, pass through a cuboidal transition during continued ageing as a result of an increasing β/ω-misfit. These particles serve as preferential α-nucleation sites, enabling very fine and homogeneously distributed α-precipitates. A recent study by Ahmed et al. (2015) on Ti-5Al-5Mo-5V-2Cr-1Fe detected fluctuations in the Mo-content of the matrix but they could not be correlated to ω- and α-precipitates that had formed during fast cooling from 1073 K. Here, compositional variations between α- and β-phase
appeared concurrently with the growth of α-precipitates during the following slow heating to an ageing temperature of 923 K.

First principle calculations show that the ω-phase is a metastable intermediate step within the β- to α-phase transformation. (Nishitani, Kawabe & Aoki 2001). Nucleation of α-phase can occur on dislocations, vacancies, grain boundaries, or on another phase, such as the ω-phase. In many near-β alloys quenched from temperatures above their β-transus, athermal ω-phase is precipitated. With subsequent ageing the ω-precipitates stabilise, grow and thus, serve as evenly distributed heterogeneous nucleation sites for the precipitating α-phase. (Ohmori et al. 2001). By this ω-assisted heterogeneous nucleation a relatively large number of fine-scaled α-precipitates are formed and homogeneously distributed within the β-matrix. These α-precipitates often exhibit morphologies that are markedly different from precipitates nucleated from prior β-grain boundaries at higher temperatures. (Dehghan-Manshadi & Dippenaar 2011). However, the exact part ω-precipitates play with respect to the nucleation of α-phase in the β-phase of titanium alloys is still under discussion.

The mechanism describing the role of ω-precipitates on nucleation of α-precipitates and the influence of ω/β-misfit and alloying element diffusivities is currently being in the literature. Two schools of thought are being put forward in an attempt to unravel the mechanism of the β+ω -> β+α-transformation. The first direction aims to describe α-formation at a certain distance from ω-precipitates due to an outward diffusion of Al from previously formed ω-precipitates. Thus, these regions can be understood to enhance α-nucleation due to a beneficial solute content. From there on the α-precipitates grow to consume the ω-precipitates. The second direction of thought describes α-precipitation to occur directly on ω/β-interfaces due to an increased dislocation density in the phase boundary area. Here, the increased lattice fault density makes nucleation favourable. Due to the nucleation of α-phase on the interface a mutual orientation relationship with α-, ω- and β-phases exists.

Williams and Blackburn (1969) found that Ti-20V, a system with a high β/ω-misfit, shows a tendency for nucleating α-phase as fine rods on ledges or dislocations at the β/ω-interface. These rods are diagonally oriented with respect to the cubical ω-faces, parallel to <110>β. During ageing these rods combine, consuming the ω-phase. A
study of Ti-10V-2Fe-3Al by Duerig, Terlinde and Williams (1980) confirms these results but also highlights a correlation with ageing temperatures and times. Here, fine and uniformly distributed α-phase formed at low ageing temperatures typically less than 723 K with a similar distribution in respect to the prior existing cuboidal ω-precipitates, indicating nucleation of α- at ω-precipitates. Following this type of α-nucleation a second non-uniformly type of nucleation occurred with no apparent relationship to the prior existing β- and ω-phases. This clustered type of α-precipitation is most likely a self-energised process where new α-precipitates are formed from previously existing α-precipitates. In addition, increased α-formation along grain boundaries occurred at this stage. By increasing temperatures to 923 K the grain boundary α-precipitation becomes the predominant nucleation mechanism. (Duerig, Terlinde & Williams 1980). These findings are supported by a TEM study of Ohmori et al. (2001) on Ti-10V-2Fe-3Al, which captured early stage nucleation of α-laths at the ω/β-interface. They showed that the nucleating α-phase has a coherent interface with very small misfit along $(10\bar{1}0)_\alpha || (1\bar{1}00)_\omega$. They conclude that the growing α-phase consumes the ω-particle as it maintains a coherent interface in between them. Thus, if heat treatment parameters promote a fine and homogeneous distribution of ω-precipitates of various orientations, the resulting α-phase will also consist of fine, uniformly distributed α-precipitates of various orientations. (Ohmori et al. 2001).

The situation in low-misfit systems appears to be less clear. Azimzadeh and Jack (1998) found similar results for Ti-6.8Mo-4.5Fe-1.5Al, a low-misfit alloy, as presented above by Duerig, Terlinde and Williams (1980) with regard to type and morphology of α-nucleation and its dependence upon the ageing temperatures and time. However, they also argue that α-phase nucleates preferentially a little distant from the ω/β-interface (based on an assumed compositional variation of Al within this distance to the ω/β-interface) thereby accelerating α-precipitation in this region through a beneficial alteration in solute type and amount as compared to the general alloy composition. These assumptions were supported through a study by Nag et al. (2009) on Ti-5Al-5Mo-3Cr-0.5Fe. They were able to show that coarse ω-precipitates formed during ageing at 623 K that were slightly depleted in Al. The α-precipitates
that had formed in the vicinity of these ω-precipitates were found to be slightly enriched in Al. Thus, indicating that α-precipitation occurred with a slight distance to the ω-precipitates due to a solute content closer to the equilibrium α-phase and thus energetically favoured due to the reduced necessity of diffusion. These findings were confirmed in a recent study on Ti-5Al-5Mo-5V-3Cr. (Coakley et al. 2015). A similar study on the same alloy by Jones et al. (2009) is employing synchrotron radiation to follow the phase transformations in-situ during the heat treatment. They showed the appearance of peak-shoulders on ω-peak positions next to β-peaks which start reducing after α-phase has formed in a sequence of powder diffraction patterns. Hence, indicating that α-nucleation and subsequent growth is interrelated with the dissolution of ω-precipitates. Outcomes of a study of a Ti-11.5Mo-6Zr-4.5Sn alloy showed that α- and ω-phase coexist over long ageing times. (Feeney & Blackburn 1970). A TEM study of a Ti-6.8Mo-4.5Fe-1.5Al alloy by Prima et al. (2006) confirmed the coexistence of α- and ω-phase and suggests (as opposed to (Azimzadeh 1998)) that α-formation in low-misfit systems occurs within the core of ω-particles, leading towards their dissolution and the subsequent growth of the α-precipitate into the β-matrix. In line with this theory Langmayr et al. (1994) suggested a two-step nucleation and growth process. Based on data from Small Angle X-ray Scattering experiments on single crystals of Ti-12Mo, they showed that the longer axis of α-platelet-nuclei matches with the longer axis of ellipsoidal ω-precipitates. Thus, a fast, diffusionless ω- to α-phase transition is followed by relatively slow diffusionally driven growth of the α-phase - into the matrix. (Langmayr et al. 1994).

Many of the studies outlined above did not consider the formation of an α”-phase. The α”-phase can be considered as a transitional phase, which exists before the occurrence of the α-transformation since it requires lattice strains in the same directions as the transformation of α- from β-phase, but smaller in magnitude. Thus, it forms preferably in alloys where the direct formation of the hexagonal structure is hindered by chemical stabilisation of the transforming β-matrix. (Duerig et al. 1982). A Ti-7Mo-alloy formed α”-phase upon quenching, which decomposed into solute-enriched α”- and α-precipitates during subsequent annealing. (Bagariatskii, Nosova & Tagunova 1958). Similar results were obtained by Davis, Flower and West (1979a)
in a Ti-4-8 wt.%Mo alloy. A spinodal decomposition was responsible for the changes in solute content of α”-phase. Upon ageing α”-phase decomposed into β-phase, which then immediately formed α-precipitates in a β-matrix. Barriobero-Vila et al. (2015b) employed high energy X-rays to investigate the phase transformation sequence in a Ti-10V-2Fe-3Al alloy as a function of the applied heating rate. This alloy consists of α”-precipitates in a β-matrix upon quenching and may also contain ωα-phase. Their findings show that during slow heating at a rate of 5-20 K/min, ωiso-phase is formed from the β-matrix by a diffusion-controlled mechanism. For every heating rate β-phase was found to form spontaneously from α”-phase through a reverse martensitic reaction at ~473 K. The extent of the reverse reaction increased with the heating rate. In case of the fastest heating rate 50 K/min, α”-phase completely transforms into β-phase and was also found to be involved in the ωiso-formation. With further increasing temperatures these phase transformations were found to reverse again so that α”-phase is formed from the β- and ω-phases accordingly. Their findings on the phase transformation sequence was supported through the lattice parameter evolutions for the different phases in the three heat treatment conditions. For example based on crystal structure considerations between ω- and α”-phase the interrelation between ω- and α”-lattice parameters indicates an α”-to ω-phase transition, followed by the reverse process. Finally, they conclude that α-phase will be formed within α”-martensite plates, from α”-particles and also the β-phase. The ω-phase does not play a direct role in the α-formation of this alloy because it dissolves during the α”-transition. (Barriobero-Vila et al. 2015b).

3.3 Open Questions with Regard to Phase Transformations in Near-Beta Titanium Alloys

Section 3 highlighted the complexity of the underlying mechanisms in the β- to α-phase transformation in near-β-titanium alloys. Alloy composition in combination with the chosen heat treatment parameters can determine the phase transformation sequence and thus, the mechanism of α-phase transformation. Therefore, current research needs to determine exact phase transformation sequences and mechanisms as influenced by the heat treatment parameters and alloy composition. The role of intermediate phases such as ω- and α”-phase and their interrelation with respect to
α-nucleation and growth, including the effect on α-transformation kinetics requires further investigation. Only then it will become possible to predict the microstructure and thus the properties of alloys with different compositions following thermo-mechanical processing. In order to address these issues the use of in-situ techniques and suitable analysis procedures have become increasingly important as they allow tracking phase changes and the evolution of new phases in real time and at temperature. In addition, the influence of lattice strains and compositional effects on lattice parameters can be studied in detail.
4 Diffraction Theory Pertinent to the Present Investigation

Diffraction transforms the atomic structure of a crystal into a diffraction pattern in reciprocal space. With the information contained in this pattern it is possible to model the three-dimensional distribution of atoms in a crystal lattice in real space and verify these models by transforming them into reciprocal space. (Pecharsky & Zavalij 2005, p. 100). Diffraction pattern contain information on lattice parameters and strains, phase compositions and fractions, grain size and many more. By recording diffraction pattern in-situ during thermo-mechanical processing it becomes possible to investigate the mechanisms of material processes such as deformation, recovery, grain growth or kinetics of phase transformations. Therefore diffraction methods represent a powerful technique for material science. (Liss & Yan 2010).

4.1 Basics of diffraction

In order to understand the opportunities and limitations of diffraction techniques it is instructive to briefly outline the basic underlying theory. Diffraction sources were used in the present study and although the unique features of neutron-, electron- and high-energy X-ray- diffraction techniques can be utilized to obtain different pieces of information, the underlying physics are the same in all cases. To understand why different diffraction methods produce a different set of diffraction patterns, it is useful to visualise diffraction. In general, there are two types of scattering, elastic and inelastic. In the case of elastic scattering the scattered beam has the same wavelength as the incident beam which means that there is no energy transfer between wave and sample. On the other hand for inelastic scattering the wavelength of the scattered beam is changed according to the direction of the energy transfer to or from the sample. That is the sample loses or receives energy. (Pecharsky & Zavalij 2005, p.102). The current study is based on diffraction techniques employing elastic scattering so that the theory underpinning inelastic scattering is not relevant in the present discussion.

In the case of infinitely large crystals Bragg’s law in Equation (12) and illustrated in Figure 20 needs to be fulfilled as a criterion that diffraction is enabled. (Pecharsky & Zavalij 2005, p.148).
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\[ n\lambda = 2d_{hkl}\sin\theta_{hkl} \quad (12) \]

Bragg’s law states that diffraction is only possible if the incoming wave has a wavelength \( \lambda \) of the same order of magnitude as the repetitive distance between scattering objects, which in this case means atomic planes of a certain hkl. Therefore if an incoming wave (wave vector \( k_i \) where \( k \) is defined as in Equation (13)), hits an atomic plane \{hkl\} at a specific angle \( \theta_{hkl} \) the reflected wave with a wave vector \( k_f \) will have a path difference, \( \Delta \), that allows for constructive interference. Thus, the diffracted intensities can be detected under an angle \( 2\theta_{hkl} \) to form a diffraction pattern, which has unique characteristics for each diffraction method used. (Pecharsky & Zavalij 2005, p.148). This enables the definition of the scattering vector \( Q \) as shown on the top of Figure 20 as the difference between the incoming and the outgoing wave vectors (Equation (14)). (Copley 2001, p. 3). The given example is a special value of \( Q \) where constructive interference occurs in which case \( Q \) is expressed as \( G_{hkl} \). (Copley 2001, p. 5).

\[ k = \frac{2\pi}{\lambda} \quad (13) \]

\[ Q = k_f - k_i \quad (14) \]
Diffraction Theory Pertinent to the Present Investigation

In the case of elastic scattering $Q$ can be calculated from Equation (15). (Copley 2001, p. 3).

$$Q = 2k \sin \theta = \frac{4\pi}{\lambda} \sin \theta = \frac{2\pi}{d} \quad (15)$$

As mentioned before for special values of $Q$ constructive interference occurs in which case $Q$ can be expressed as $G_{hkl}$. These $G_{hkl}$ form the reciprocal lattice and can be expressed through the reciprocal space unit basis vectors $a^*$, $b^*$ and $c^*$ as in Equation (16). (Copley 2001, p. 5).

$$G_{hkl} = ha^* + kb^* + lc^* \quad (16)$$

The reflections $hkl$ are generally called Bragg reflections and the corresponding peaks are named Bragg peaks. The lattice spacings $d_{hkl}$ can be calculated from the scattering vector following Equation (17). (Copley 2001, p. 6).

$$d_{hkl} = \frac{2\pi}{G_{hkl}} \quad (17)$$

According to these definitions, recording of a diffraction pattern can be visualised as shown in Figure 21 and Figure 22.

Figure 21 depicts how an imaginary sphere, the Ewald’s sphere, can be used to explain formation of diffraction rings on a flat detector. For elastic scattering the incoming wave vector $k_i$ and the outgoing wave vector $k_f$ have the same wavelength with an angle of $2\theta$ between them. The wave vectors form the radius of the Ewald’s sphere. Therefore, diffraction can only occur if a reciprocal lattice point lies at the end of $k_f$, on the sphere. Thus, $G_{hkl}$ has to be smaller or equal to $2k$ for the lattice planes ($hkl$) to diffract the incoming wave. If the specimen under consideration is fine powder or fine-grained material without preferred orientation $G_{hkl}$ form a continuous circle on the surface of the sphere perpendicular to $k_i$. If the outgoing wave vectors $k_f$ belonging to that $G_{hkl}$ were extended to form a cone it can be seen that they would intersect a flat detector arranged perpendicular to $k_i$ in the shape of a ring, the Debye-Scherrer ring. (Pecharsky & Zavali 2005, p.153).
Figure 21: Schematic representation of the diffraction mechanisms for recording a Debye-Scherrer ring on the detector. (Pecharsky & Zavalij 2005, p.153).

Figure 22 shows the possible distribution of diffraction cones for different hkl in the case of a copper alloy. In the case of good grain statistics (that is a high number of grains per sample) which show no preferred grain orientations the diffracted intensity is constant around the circumference so that it may not be necessary to measure the entire ring. The measured intensity can be integrated along (part of) the ring to form the commonly known powder diffraction pattern where intensity is plotted vs. 2θ, d-spacing, Q, etc. (Pecharsky & Zavalij 2005, p. 154-155).

Figure 22: Schematic representation of diffraction cones of a polycrystalline copper sample intersecting an area detector. (Pecharsky & Zavalij 2005, p.155).

As mentioned before, diffraction data is generally expressed as a function of the scattering angle 2θ, the lattice spacing d or the scattering vector Q. The most common method is to plot the intensity of the diffracted beam vs. 2θ. However, 2θ
is dependent on the wavelength and therefore, the instrument setup. For reasons of comparison and to improve presentation quality it is convenient to plot intensities against either real properties of the material such as lattice spacings or the scattering vector (since Q represents values in reciprocal space where the diffraction pattern originate). Therefore, in this study diffraction data will mostly be plotted against Q.

### 4.1.1 Interaction of Radiation with Crystals

Either the kinematic or dynamical theory of diffraction is usually employed to describe the interaction of radiation with crystals. The kinematic theory of diffraction assumes negligible interaction between the diffracted beam and the crystal which is true for a small interaction between radiation and crystal or for relatively thin crystals. On the other hand for a strong interaction multiple scattering of the diffracted beam as well as other interactions with the crystal are taken into account in the dynamical theory of diffraction. The mathematics behind the dynamical theory are rather complex and hence this theory would only be used when dealing with almost perfect crystals. The kinematic approach is mathematically much simpler and would generally suffice for describing diffraction phenomena in polycrystalline materials. (Pecharsky & Zavalij 2005, p. 102-104).

As mentioned at the beginning of this Section, significant differences exist between the radiation types used in this study. Thus, each diffraction method produces a different set of diffraction patterns which render them useful for studying different aspects of material science and therefore useful as complimentary tools. The main difference of the relevant neutron, synchrotron and electron diffraction techniques for this study lies in the way the radiation interacts with the material. X-rays and electrons interact with the electron cloud of atoms which makes up most of the atomic volume. Hence, the interaction between radiation and sample is very high, making small or thin samples a requirement for these techniques to work. Additionally, as the electron cloud volume increases with increase in atomic number the interactions are stronger for heavier elements than for lighter elements. Neutrons on the other hand interact with the nuclei of atoms which makes up only a very small amount of the atomic volume. Due to the low interactive volume of
Diffraction Theory Pertinent to the Present Investigation

neutrons they can be used for bigger samples compared to the other two techniques. Thus, the grain statistics of materials such as β-titanium alloys which can have grain sizes of more than 1 μm are significantly improved when using neutrons. In addition, the interaction of neutrons is independent of the atomic number. Instead the interaction is defined through the bound coherent scattering cross section of the material $\sigma_c$ which is dependent on its bound coherent scattering length $b_c$ as given in Equation (18). (Prince 2006, p. 452).

$$\sigma_c = 4\pi|b_c|^2$$  \hspace{1cm} (18)

This scattering length for a material is dependent on the sum of products of the mole fraction $X_i$ of the isotope with its respective scattering length (Equation (19)). These scattering lengths can vary strongly even between isotopes. (Prince 2006, p. 453).

$$b_c = \sum_i X_i b_{ci}$$  \hspace{1cm} (19)

Table 4 lists scattering lengths for elements that are typically used in alloying of titanium. It can be seen that titanium has a negative scattering length while other elements such as aluminium which is used in almost every titanium alloy possess a positive scattering length. From Equation (19) follows that certain compositions would lead to a titanium alloy with a scattering length and consequently a scattering cross section close to zero which would result in that alloy being “invisible” to neutrons. Thus, it should be understood that the solute content of a titanium alloy will affect the strength of the detected neutron diffraction signal.

Table 4: Scattering lengths of titanium and common alloying elements. (Prince 2006, pp. 445-452).

<table>
<thead>
<tr>
<th>Element</th>
<th>Ti</th>
<th>V</th>
<th>Al</th>
<th>Fe</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>$b_{ci}/\text{fm}$</td>
<td>-3.37</td>
<td>-0.38</td>
<td>3.45</td>
<td>9.45</td>
<td>6.72</td>
</tr>
</tbody>
</table>
4.2 Principles of Diffraction Data Analysis

A diffraction pattern is a reciprocal space record of the atomic structure of a material. It can be described as an interference pattern resulting from superimposed waves. Mathematically, this process can be described by a Fourier transformation. By interpreting this pattern in reciprocal space conclusions on the atomic structure of a material can be made. (Pecharsky & Zavalij 2005, p. 100).

Full Debye-Scherrer rings recorded of an ideal powder or a small-grained material with completely random crystallite orientations possess a uniform intensity distribution along the rings. By integrating the intensities azimuthally along the ring the powder diffraction pattern are formed. (Liss & Yan 2010). However, if the crystallite orientations are not fully random integrating along the ring will lead to the loss of information on preferred orientations or texture. Thus, by plotting the intensity distribution of a ring over its azimuthal angle and time, conclusions on material processes such as grain growth, recovery or recrystallization can be made. (Liss et al. 2006; Liss & Yan 2010).

In general, the following characteristics are relevant to powder diffraction patterns: The background originates from the sample environment as well as diffuse scattering from the sample. The peak positions depend on the type and dimensions of the unit cell. The peak intensities are related to the type and location of atoms in the unit cell. Finally, the peak profiles are influenced by the instrument characteristics and microstructural parameters of the sample such as crystallite size and strain. (Dinnebier & Billinge 2008, p. vi)

Depending on the type and amount of information that is required, different approaches can be taken to analyse the diffraction pattern. If the atomic structure is not to be fully modelled, single peak fitting can be a good choice for data analysis. It is a time-saving technique and can usually be semi-automated by using computer macro scripts, so that even large amounts of data can be analysed within a reasonable timeframe. However, when results are strongly affected by structural considerations the Rietveld method is preferred since it takes the full atomic structure of the material into account.
4.2.1 Principle of Single Peak Fitting

In this method individual or multiple peaks are fitted simultaneously but independently by an analytical function to gain crystallographic information on peak positions, intensities and/or shape of some of the peaks instead of the full pattern. Software used to run these peak profile refinements will usually fit a mathematical function to the peak and improve the fit through a least-square refinement in which the residual $M$ of Equation (20) is minimised, where $y_{io}$ and $y_{ic}$ are the observed and calculated intensities at point $I$ respectively. (Chateigner 2010, p.12).

$$M = \sum_i \frac{1}{y_{ic}} (y_{io} - y_{ic})^2 \quad \text{(20)}$$

Functions commonly used to describe the profiles are Gaussian, Lorentzian, Voigt and the pseudo-Voigt functions. As this method uses a mathematical best fitting approach without actual physical meaning its usefulness is limited to gathering information without too much structural interdependence and requires sufficient experience of diffraction data to create meaningful results. However, an advantage of the method is that results can be gathered quickly and with a focus on the relevant information. (Chateigner 2010, p.12).

4.2.2 Principles of the Rietveld Technique

When the required information is strongly dependent on the structural information of the material a complete structural refinement using the Rietveld technique may become necessary. Here, an atomic model containing space group, lattice parameters and atomic positions as well as instrument parameters and wavelength are entered into the software which will fit the profile function and background to the whole set of experimental data. The refinement will usually improve scaling, zero off-set, thermal motion, the profile shape (using the same mathematical functions as in the single peak fitting technique) and atomic positions to refine space group, lattice parameters, atomic coordinates, and/or the wavelength for a better fit of the calculated model to the data. (Chateigner 2010, p.41-42).
An advantage of this technique is that the powder diffraction pattern is refined as a whole using a physically meaningful model. Each point of the pattern including background and overlapping peaks are refined through a least-square refinement following Equation (20) to improve the fit of function to data. So that peak intensities are modelled for a whole phase and not just separate peaks. (Chateigner 2010, p.41-42). However, this also presents a disadvantage of the technique as it requires experience to choose models that are suitable in describing actual sample properties and do not simply improve the fit without creating meaningful results. To gain this experience much more time is required as compared to the single peak fitting method to find the best models and suitable parameters thereof in describing the sample properties.

Nevertheless, once the technique is applied correctly it enables the determination of phase fractions, grain sizes, lattice strains and texture with models that consider phases as a whole, which renders it a very valuable tool for studying material processes such as phase transformations. (Chateigner 2010, p.41-42)
5  Research Plan and Experimental Methods

Samples of the near-β titanium alloy Ti-1Al-8V-5Fe have been subjected to thermo-mechanical treatments with differing temperature settings in order to investigate the material processes during the phase transformations. Neutron diffraction data was collected using the high-intensity diffractometer Wombat at the Australian Nuclear Science and Technology Organisation (ANSTO). The high-energy X-Ray studies were conducted on beamline ID15B at the European Synchrotron Radiation Facility (ESRF). Both experimental facilities enable data collection while the experiment is running so that the analysis of this in-situ data provides information on material processes, which would be difficult to achieve by conventional techniques. In order to gain information at the atomic level, samples of Ti-1Al-8V-5Fe were prepared for Transmission Electron Microscopy (TEM) observations. Firstly, in-situ TEM experiments following similar heat treatments to previous diffraction experiments have been conducted. To enable better contrasts and higher resolution for crucial steps of these heat treatments aberration corrected TEM was performed to reveal exact material processes from ex-situ prepared samples.

As mentioned in Section 4.1.1 there are significant differences between the diffraction methods used in this study. These differences make them useful for studying different aspects of materials science and therefore useful as complimentary tools. Some of the main differences of the relevant neutron, synchrotron and electron diffraction techniques for this study are summarised in Table 5.

Table 5: Major characteristics of diffraction methods applied in this study (Pecharsky & Zavalij 2005, p. 114)

<table>
<thead>
<tr>
<th></th>
<th>Neutrons (High-Intensity)</th>
<th>Synchrotron (High-Energy)</th>
<th>Electrons (TEM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scattering</td>
<td>By nuclei, very small interactions,</td>
<td>By electrons, high interactions,</td>
<td>By electrons, very high interactions,</td>
</tr>
</tbody>
</table>
A more detailed description of the experimental approach to investigate the heat treatment response of the near-β titanium alloy Ti-1Al-8V-5Fe is given in Sections 5.2 and 5.3. Before that, the material properties of the Ti-1Al-8V-5Fe alloy are introduced in Section 5.1.

### 5.1 The near-β titanium alloy Ti-1Al-8V-5Fe

The main focus of the current study was to unravel the mechanisms by which the α-phase precipitates during ageing treatments of the titanium alloy Ti-1Al-8V-5Fe. The beta-transus of this alloy is 1103 K. (Collings, Boyer & Welsch 1994, p. 993). This near-β titanium alloy exhibits excellent hardenability and strength characteristics combined with high fracture toughness and excellent high-cycle fatigue behaviour and can be used to manufacture aerospace fasteners or used in other high strength
applications. (Collings, Boyer & Welsch 1994, p. 993-998). The exact composition of the alloy is given in Table 6.

Table 6: Exact composition of Ti-1Al-8V-5Fe

<table>
<thead>
<tr>
<th>Al/ wt-%</th>
<th>V/ wt-%</th>
<th>Fe/ wt-%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.13</td>
<td>7.89</td>
<td>4.97</td>
</tr>
</tbody>
</table>

Joshi et al. (2013) have shown that this alloy can be produced through a low-cost powder metallurgical route. However, little is known about phase transformations that occur in this alloy and the only isothermal time-transformation-temperature diagram that could be found is shown in Figure 23. It can be seen that it is somewhat incomplete as only equilibrium phases are considered and only three temperatures were measured to estimate the time and temperature for the β- to α-phase transformation. The equilibrium phases were obtained from samples that had been solution treated for 30 min at 1228 K, water quenched and then reheated and held for varying times at three different temperatures. The lowest temperature at which α-phase is detected was ~703 K and required 2000 s of holding time. At a temperature of ~763 K the α-transformation is accelerated so that a holding time of 1000 s was sufficient to precipitate α-phase. Thus, for the purposes of obtaining results in a reasonable time frame, ageing temperatures in excess of 763 K were used in the current in-situ studies.

Figure 23: Isothermal TTT diagram obtained from solution treated samples that were held for varying times at three different temperatures
A Mo-equivalent of [Mo] ≈ 16.6 wt% for the Ti-1Al-8V-5Fe alloy was calculated by Equation (5) while Equation (6) rendered an $M_s$-temperature of 135.5 K. Thus, upon quenching no $\alpha'$-phase would be expected to form in this alloy and the $\beta$-phase should be retained. Due to the high amount of the $\beta$-stabilisers V and Fe it would be expected that even at optimal $\alpha$-precipitation conditions a large fraction of $\beta$-phase will be retained in heat treatments. That is because the maximum solubilities for the $\beta$-stabilisers in the $\alpha$-phase are with about 3 % V at 953 °K comparatively high but extremely low in the case of Fe with maximal ~0.5 % solubility. (Lütjering & Williams 2007, p. 26-27). These solubilities are further reduced at lower temperatures so that at the chosen experimental $\alpha$-ageing temperatures of 763 to 823 K an outward diffusion of $\beta$-stabilisers from $\alpha$-precipitates into the matrix would be expected, leading to a $\beta$-phase significantly enriched in $\beta$-stabilisers. Hence, a significant amount of $\beta$-phase will be stabilised at $\alpha$-ageing temperatures.

As was detailed in Section 3.1.2 the diffusion rates of Fe are comparable to interstitial alloying elements in both the $\beta$- and $\alpha$-phase (see Figure 16). Also shown was that Fe affects other substitutional element diffusivities such as Al in the $\alpha$-phase so that diffusion related processes can be expected to possess very fast kinetics in this alloy in particular in the $\alpha$-phase. This should have a significant effect on the phase transformation behaviour and kinetics in this alloy and shall be compared to studies presented in Section 3.2.2 on other near-$\beta$ titanium alloys. By comparing those findings it will be possible to conclude on the influence of diffusion rates on the phase transformation mechanisms in near-$\beta$ titanium alloys.

Samples of the Ti-1Al-8V-5Fe alloy for the in-situ studies were prepared as follows: Rods with a diameter of 8.9 mm were cut to a length of approximately 13.2 mm for use in the neutron diffraction experiments. For the synchrotron studies these cylinders were wire-cut to cylinders of 3 and 4.5 mm in diameter with a length of 6 and 9 mm respectively. The neutron diffraction samples were encapsulated under vacuum in quartz tubes and then heat treated for half an hour at 1173 K in a conventional furnace and water quenched to ensure a fully developed, but metastable, $\beta$-phase as the initial microstructure at the start of each experiment. Thin foils for in-situ STEM investigations were produced from these cylinders as follows:
They were cut to produce discs of approximately 200 µm thickness, from which 3 mm discs were punched and then polished to 80 µm thickness. These discs were dimpled to about 30 µm thickness in the centre of the disc before ion milling on a Gatan PIPS-691 Ion-Mill with 5 keV under an angle of 6˚ and a gun current of 15-20 µA. Heat treated discs, approximately 300 µm thick, were processed in the same way to produce thin foils used in the ex-situ HRSTEM investigations. Details of these heat treatments are given in Section 5.3.2.

5.2 Neutron and Synchrotron Diffraction Studies

Due to the differences in diffraction mechanisms between neutron and high-energy X-rays detailed in Section 4.1.1, both methods are advantageous for studying different aspects of the pertaining phase transformations and hence, both have been used in a complimentary fashion.

Since the neutron technique employs bigger samples, the information gained provide better grain statistics so that for example, determined lattice parameters should have a higher accuracy. For neutrons the scattering length is independent of the atomic number of the material so that effects resulting from diffusion of alloying elements can be investigated through intensity changes. On the other hand, high-energy X-rays allow recording intact Debye-Scherrer rings covering a high Q-range so that effects such as grain growth can be observed by studying their development over time. Also high-energy X-rays have higher data acquisition times than neutrons, which enable the collection of meaningful data of the phase transitions during heating at high heating rates of 100 K/min. By combining the information from these different techniques with analysis such as line profile analysis, single peak fitting and Rietveld refinement as detailed in Section 4.2, it is possible to study the heat treatment response of a material in detail. Hence, changes in grain size, orientation as well as lattice strains can be observed and in addition, recovery, recrystallization and phase developments in the course of an experiment can be made. (Liss & Yan 2010).

5.2.1 Neutron diffraction studies on Wombat

Neutron diffraction experiments were conducted on Wombat, the high-intensity powder diffractometer at ANSTO. (Studer, Hagen & Noakes 2006). The goal of these
studies were to assess the mechanism by which the α-phase nucleates in near-β titanium alloys as a function of heating rate and ageing temperature in addition to studying isothermal ageing behaviour. As mentioned before, by using neutrons information on bulk behaviour of relatively large samples can be collected, which improves the grain statistics of the gathered information.

The general experimental setup is shown in Figure 24. For the purposes of this study the neutrons were monochromised with a Ge monochromator to a wavelength of 2.42 Å. The sample stage held the 1600 °C ILL-type vacuum furnace shown on the left of Figure 25. The sample is fixed to a sample stick in close proximity to a thermocouple which allows recording the sample temperature while also placing the sample into the centre of the furnace and thus the incoming neutron beam. The sample will diffract the incoming beam as incomplete Debye-Scherrer rings measured on the 120˚ area detector. The comparatively high speed of data acquisition on Wombat enables the acquisition of one pattern per minute which is sufficient to follow the structural changes in the sample in-situ during the heat treatment. With the chosen experimental settings the scattering vector will cover a Q-range of 2.2-4.9 Å⁻¹ which includes the first three β-peak positions and more for the other relevant phases.
Figure 24: Wombat setup at ANSTO (ANSTO)

The furnace uses two vacuum pumps to ensure a high vacuum of about $10^{-5}$ Pa suitable to avoid sample oxidation under the chosen heat treatment parameters. Figure 25 shows the disassembled furnace and its controlling unit. The Nb-heating elements inside the furnace also diffract the incoming neutron beam so that depending on the positioning of furnace and detector toward the incoming beam the signal from the sample environment can be stronger or weaker and in case of overlap with peak positions of the sample disturb the measurement. Therefore, the detector position needs to be optimised at the beginning of the experiment to reduce the signal from the sample environment.

Figure 25: Left: 1600 °C ILL-type vacuum furnace; Right: Furnace controller

As explained in Section 4.1 diffraction from a particular family of lattice planes will occur in the shape of a cone which intersects the detector as a circle, the Debye-Scherrer ring of that particular hkl. While this holds true for the high-energy X-ray data, in neutron diffraction only a relatively small part of the circular arc of the diffracted beam is captured by the detector due to the differences in energy levels of the two methods. The detected intensity is integrated along this part of the ring and plotted in a diffraction pattern as intensity vs. the scattering vector $Q$. These patterns can then be analysed through single-peak fitting techniques or Rietveld analysis as detailed in Section 4.2.

The heat treatment used in the first set of experiments of the Ti-1Al-8V-5Fe alloy is outlined in Figure 26. As explained at the end of Section 5.1 all samples were heat
treated for half an hour at 1173 K in a conventional furnace and water quenched to ensure that a fully developed β-structure is retained. The ageing treatment in step II was done on Wombat within the temperature-regulated vacuum furnace detailed previously (Figure 25). As was detailed in Section 3.2 the combined effects of composition and heating rates determine the sequence and extent of intermediate phase transformations. By varying the heating rate between 1 K/min and 20 K/min it was possible to obtain or avoid intermediate ω-phase precipitation in this alloy and thus to investigate the influence of ω-phase on α-phase precipitation at an ageing temperature of 823 K. Studies by Zheng et al. (2016c) have shown that the occurrence of an intermediate ω-phase precipitation will have a significant effect on the morphology and distribution of the α-phase in the β-matrix and thus the final mechanical properties. The effect of heating rate on phase transformation behaviour and α-morphology will be compared to outcomes of similar studies within Section 6.1

Figure 26: Heat treatment of Ti-1Al-8V-5Fe samples investigated on Wombat

In a subsequent Wombat experiment, the heat treatment shown in Figure 27 was imposed in order to determine the effect of an intermediate holding temperature on ω-precipitation and α-phase development at 823 K. The heating rate to the holding temperatures was kept constant at 20 K/min. The outcomes of both types of experiments had been analysed using batch-mode Rietveld refinement within the software ‘Materials Analysis Using Diffraction (MAUD)’ (Lutterotti 2011). These analyses were aimed at determining the influence of heat treatment parameters on phase fraction and lattice parameter development to investigate the phase
transformation kinetics while also looking at the role of diffusion in the different transition stages.

![Figure 27: Heat treatment including an isothermal holding step at \(\omega\)-precipitation temperatures](image)

### 5.2.2 Synchrotron Studies at ESRF

The high-energy X-ray studies were run on the high energy beamline ID15B at ESRF. The incident beam has a wavelength of \(\lambda = 0.14\ \text{Å}\) at an energy level of \(E = 87.17\ \text{keV}\). This highly brilliant beam allowed investigations on cylindrical titanium samples of up to 4.5 mm in diameter. The operating principle of the ESRF setup is shown in Figure 28. The sample is mounted into the load frame and diffracts the incoming beam in a cone shape which intersects the 2D detector as full Debye-Scherrer rings.

![Figure 28: Operating principal of the experimental setup at ID15B: Incoming beam is diffracted in cone shape which intersects detector as Debye Scherrer rings. (Liss & Yan 2010)](image)
These rings contain a lot of information on the studied material such as grain size or orientation relationship. Thus, by studying the development of these variables over time as influenced by the imposed heat treatment parameters, it becomes possible to investigate grain development. For a conventional powder diffraction analysis the intensity is integrated along the ring and plotted in a diffraction pattern as intensity vs. $Q$. An advantage of the high flux of high-energy x-rays is that it provides excellent resolution, which allows improved peak separation within the diffraction pattern. Compared to the Wombat experiments the covered $Q$-range is increased to $2.1 – 7.7 \text{ Å}^{-1}$, thus enabling recording of a higher number of peaks for each phase. In addition, data is recorded at a higher rate, which improves the density of data points at higher heating rates so that even measurements at 100 K/min could be followed successfully. (Liss et al. 2003).

The sample environment at the ID15B beam-line illustrated in Figure 29 is essentially a Gleeble thermo-mechanical simulator. For the purposes of the present investigation the instrument had been set up for compressive testing and a loaded sample is shown in the zoom in Figure 29. The sample chamber was insulated and flushed with argon gas to create an inert atmosphere and thus, avoid excessive oxidation of the induction-heated samples. The temperature profile was recorded through a spot-welded thermocouple and in addition the anvil movement and the applied load were recorded. This data was linked to the recorded Debye-Scherrer pattern, thus enabling an effective and accurate link between the thermo-mechanical parameters and the measured diffraction data.
Similar heat treatment parameters used in the neutron diffraction experiments, outlined in Figure 26, were used for the synchrotron experiments on the Ti-1Al-8V-5Fe alloy. Here, the samples were solution treated in-situ at 1173 K for about 5 min before fast-cooling to room temperature and then heated continuously by 5 or 100 K/min to the ageing temperature of 823 K.

5.3 TEM studies

Due to the thinness of TEM samples combined with an energy level of the incoming electron beam of 200 keV it becomes possible to investigate materials on the atomic scale which offers valuable, complimentary insights to the other two techniques.

5.3.1 In-situ TEM studies

Pre-selected heat treatments (similar to those used in the previously detailed diffraction experiments) were conducted on a JEOL JEM-2200FS transmission electron microscope at ANSTO. Here, the maximum ageing temperature was limited by the setup so that the samples were heated continuously by 5 or 20 K/min to 763 K. The focus of these in-situ experiments was to record selected area diffraction (SAD) pattern evolutions from suitable zone-axes during the heat treatment. It is envisaged that this additional diffraction technique will allow for phase identification that
cannot be commonly observed in the other diffraction methods such as athermal \( \omega \)-phase and thus, compliment the previous techniques.

### 5.3.2 Ex-situ HRSTEM studies

The *ex-situ* High Resolution Scanning Transmission Electron Microscopy (HRSTEM) investigations using a JEOL JEM-ARM200F at the University of Wollongong aimed at gaining insights into mechanisms of the phase transformations at chosen points within the heat treatment on an atomic level. Therefore, samples were sourced from selected points in the heat treatments outlined in Figure 26 and Figure 27. Small discs, 300 \( \mu \)m thick were cut from solution treated and water quenched specimens. They were then heat treated *in situ* under an inert atmosphere within a high-temperature laser- scanning confocal microscope at the University of Wollongong in which high cooling rates could be achieved. Thin foils were prepared from these samples as explained in Section 5.1. Orientation relationships were determined between the respective phases at different stages in the transformation processes. Also, high resolution elemental maps were constructed for regions of interest, which in combination with recorded STEM bright field and dark field images provide information on elemental distributions in the different phases. Through a Fourier analyses of high-resolution images it was possible to investigate precipitation on a nanometre scale, to study the atomic structure of phase boundaries and thus to determine the development of lattice strains as a result of precipitation.

The combination of these different techniques is envisaged to enhance understanding of the open questions identified in Section 3.3 in regard to the \( \beta \)- to \( \alpha \)-phase transformation in near-\( \beta \) titanium alloys.
6 Results and Discussion

The aim of the current study is to investigate the influence of heating parameters on the β- to α-phase transformation in the near-β titanium alloy Ti-1Al-8V-5Fe. The results from in-situ diffraction studies employing neutrons, high-energy X-rays and electrons are presented in Section 6.1. These data enabled the determination of α-phase precipitation kinetics as a function of a variety of heat treatment conditions. The analysis of the transformation kinetics is discussed together with other important aspects of the β- to α-phase transformation as part of Section 6.3. Selected specimens were subjected to further investigation at atomic-level resolution using aberration-corrected Transmission Electron Microscopy (TEM). The results of the TEM study are discussed in Section 6.2. It is intended that the ex-situ TEM investigations will shed some light on the nucleation and growth mechanisms of the respective phases by revealing atomic arrangements and compositional variations across the phase boundary area.

6.1 In-Situ Diffraction Studies

The in-situ experiments were designed to reveal the phase transformation sequence and the mechanisms involved according to the applied heat treatments. All experiments were started from the as-quenched condition from a solution treatment in the β-phase. Results for the as-quenched condition are presented in Section 6.1.1. Subsequently the samples were heated to an ageing temperature of 823 K for the neutron/synchrotron diffraction studies and 763 K for the electron diffraction studies respectively. Three different heating plans were followed to reach this ageing temperature. The influence of heating rate is unveiled by continuously heating to the ageing temperature following a slow or a fast heating rate respectively. The outcomes for a slow heating rate are presented in Section 6.1.2 and results following a fast heating rate are given in Section 6.1.3. The third plan involves fast heating to an isothermal heating step at 623 K before fast heating is continued to the final ageing temperatures. Results from heat treatments including an intermediate holding step at 623 K are presented in Section 6.1.4. The results obtained from each
method are compared to reveal the phase transformation sequence and the mechanisms involved.

6.1.1 Initial Material Condition after Quenching from Above the Beta Transus

Samples of Ti-1Al-8V-5Fe have been solution treated at 1173 K for 30 min before being water quenched to room temperature. Samples, thus treated were used as the initial state in the neutron and electron in-situ diffraction studies detailed in the Sections 6.1.2, 6.1.3 and 6.1.4. In contrast, samples used in synchrotron experiments were solution treated in-situ for 3 min at 1173 K before fast cooling to room temperature. The comparatively short holding time at 1173 K was chosen to avoid excessive creep of the small samples due to the pre-load required to hold the samples in position, which sometimes exceeded the yield strength at elevated temperatures.

This section aims to characterise the initial state of the in-situ neutron and electron diffraction experiments regarding composition, morphology and phases present. The definition of the initial material characteristics will help in developing an understanding of the change processes together with the underlying mechanisms involved in the phase transformations during the respective heat treatments in the following studies.

The diffraction pattern in Figure 30 was taken at the beginning of a neutron diffraction experiment of the initial as-quenched condition. The plot shows the measured intensities over the scattering vector Q as black markers and the Rietveld fit of the software Maud through a red line. The fitting was done following a similar approach described by Lutterotti, Vasin and Wenk (2014) and Wenk et al. (2014). The rectangular box beneath the plot shows the difference between the fit and the data. The peak positions for ω- and β-phase are marked and it is seen that only the β-phase has discrete positions in the pattern. The least square fitting (Rb) was improved from 5 % to 3.5 % by adding a background peak at Q = 4.64 Å⁻¹ indicating significant diffuse scattering around that position. A smaller background peak seems to exist at Q = 2.66 Å⁻¹ but as it did not lead to a significant improvement of the fitting it was not included. The background peaks are highlighted in yellow in the figure. Approximate
peak positions for each phase have been extracted from neutron and synchrotron diffraction experiments and are listed in Table 7.

Figure 30: Neutron powder diffraction pattern of the as-quenched condition

By comparing the background peak positions with the positions of β-reflections it appears that the left peaks lies at a slightly lower Q-value than β-110 while the right peak is positioned on the right of β-211. Background alterations are termed diffuse scattering and caused by many effects. The close proximity of those background peak positions to β-reflections suggests two explanations as the most likely causes. The existence of a β'-phase, which has the same crystal structure as the β-phase, is made up of very small precipitates of a somewhat different composition than the β-matrix, thus resulting in very broad peaks at slightly different peak positions with respect to the β-phase. The presence of β'-phase after quenching has been found before for similar alloying systems by earlier researchers. Ivasishin et al. (2005) reported slight peak splitting of β-110 after quenching and a significant increase in peak broadening during subsequent heating. However, the results from heating experiments of this
study detailed in Sections 6.1.2, 6.1.3 and 6.1.4 will show that the background peaks are observed at all temperatures without significant changes in height or position. Furthermore, a phase, which differs from the β-phase mainly through its composition should have a lattice parameter that is either smaller or larger than $a_B$, which requires both background peaks to show the same trend in their differing $Q$-values with respect to the β-peaks. Thus, the presence of a β$'$-phase represents an unlikely cause of the observed phenomenon.

Another possible origin of the background peaks lies in a displacive but uncorrelated type of short-range ordering of the β-phase leading to broad background peaks around the positions for reflections from relatively close-packed β-planes. This observation is most likely related to the properties of titanium as a group IV transition metal. It has been found that the bcc phase of titanium as compared to the hcp phase possesses a relatively high likelihood for atoms to be situated elsewhere as compared to the atomic positions dictated by the crystal structure. (Stassis, Zarestky & Wakabayashi 1978). If these deviations were random the result would be anisotropic scattering, leading to a generally increased background, whereas oriented deviations from atomic positions, for example along certain lattice directions would lead to short-range displacive ordering. In this case atoms of close-packed planes that are in close-proximity to each other would slightly diverge from their positions as a whole and thus lead to the occurrence of broad peaks of small amplitude in close proximity to the actual peak position dictated by the crystal structure. This is exactly what is observed in the diffraction patterns. The origin of these background peaks will be discussed further below and also as part of Section 6.1.2.1.

|Table 7: Approximate peak positions in reciprocal space for β-, ω-, α- and α”-phase from high-energy X-ray diffraction experiments on the Ti-1Al-8V-5Fe alloy |

<table>
<thead>
<tr>
<th></th>
<th>β-Ti</th>
<th>ω-Ti</th>
<th>α”-Ti</th>
<th>α-Ti</th>
</tr>
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<tbody>
<tr>
<td>hkl</td>
<td>Q / Å$^{-1}$</td>
<td>hkl</td>
<td>hkl</td>
<td>hkl</td>
</tr>
<tr>
<td>110</td>
<td>2.75</td>
<td>001</td>
<td>110</td>
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<tr>
<td></td>
<td>2.21</td>
<td>2.47</td>
<td>2.45</td>
<td></td>
</tr>
</tbody>
</table>
Figure 31 shows a selected area diffraction (SAD) pattern of the initial as-quenched condition taken from a \textlangle 110\textrangle_\beta\text{-zone axis}. The key diagram on the right shows positions for the \(\beta\)-phase and two \(\omega\)-variants \(\omega_1\) and \(\omega_2\). The comparison of the key diagram with the SAD pattern shows that only the \(\beta\)-phase has intensity on discrete positions and two \(\beta\)-reflections have been indexed. The observed streaking is of higher density around \(\omega\)-positions and appears to connect them with \(\beta\)-110 positions, thus running in a direction towards \(\beta\)-112. The resulting streaking is of tangential character to a circle centred on \(\beta\)-111 positions and one example has been highlighted in yellow for \(\beta\)-111.

<table>
<thead>
<tr>
<th>200</th>
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<td>112</td>
<td>3.63</td>
<td>103</td>
<td>4.68</td>
</tr>
<tr>
<td>210</td>
<td>4.14</td>
<td>022</td>
<td>3.63</td>
<td>200</td>
<td>4.89</td>
<td></td>
<td></td>
</tr>
<tr>
<td>002</td>
<td>4.41</td>
<td>200</td>
<td>4.27</td>
<td>112</td>
<td>5.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>102</td>
<td>4.68</td>
<td>130</td>
<td>4.28</td>
<td>201</td>
<td>5.07</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 31: Left: SAD pattern of \( <110>_{\beta} \)-zone axis of the as-quenched condition with \( \beta \)-phase and diffuse streaking around \( \beta-111 \), white circle on aperture position for dark field image in Figure 32; Right: Key diagram

The positioning and shape of the diffuse streaking in the SAD pattern is commonly identified as nuclei of the athermal \( \omega \)-phase (\( \omega_a \)-nuclei) in the literature (Jones et al. 2009; Nag et al. 2009). It is understood to stem from a displacive type of short-range ordering in the \( \beta \)-phase, which resembles very small regions of incompletely transitioned \( \omega \)-phase. As explained above the bcc phase of titanium shows a tendency for anisotropic lattice vibrations up to high temperatures. Stassis, Zarestky, and Wakabayashi (1978) found a dip within the phonon spectrum at \( \frac{2}{3} <111>_{\beta} \), which resembles the displacement wave of \( \omega \)-formation as detailed in Section 2.5. This observation explains the temporarily existence of lattice faults resembling incompletely transitioned \( \omega \)-phase. These distortions have been identified by Schryvers and Tanner (1991) as a possible cause of the streaking that is observed in the pattern. The reason for the incomplete transition lies in the high amount of solute content in this alloy, since Williams, Fontaine and Paton (1973) have shown that too high levels of solute will prevent a full \( \beta \)- to \( \omega \)-phase transformation during quenching.

If the \( \omega \)-phase was fully transitioned to possess the hexagonal crystal structure, the SAD pattern would show discrete reflections as indicated in the key diagram, which is clearly not the case. A dark field image from diffuse scattering in between fixed \( \omega \)-positions has been taken. The white circle in Figure 31 indicates the position of the objective aperture, which was used for the dark field image in Figure 32. The dark field image of the diffuse streaking shows randomly distributed, tiny precipitates of approximately 10 to 20 Å in diameter embedded in the \( \beta \)-matrix. This observation indicates that during quenching the phase transition from \( \beta \)- to \( \omega \)-phase started, but is incomplete. Thus, leading to a \( \beta \)-matrix with regions of incompletely transitioned \( \omega_a \)-nuclei. This assumption will be further discussed with regard to the atomic arrangements shown in Figure 35.
Figure 32: Dark field image of diffuse streaking in SAD pattern as marked in Figure 31 showing 10 to 20 Å-sized precipitates in the β-matrix.

Another zone axis that is commonly used for recording SAD patterns to determine the orientation relationships between α-, β- and ω-phases is the <113>β-zone axis. Figure 33 shows the SAD pattern for this axis from the as-quenched material. From a comparison with the key diagram on the right it is evident that the pattern confirms previous observations from the <110>β-zone axis: Intensity maxima only exist on β-positions while diffuse streaking is observed in between β-positions. In the case of the <113>β-zone axis the streaking is relatively weak and of an elliptical shape. It also indicates the presence of ω-phase nuclei. (Azimzadeh 1998; Williams, Fontaine & Paton 1973).
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Figure 33: Left: SAD pattern of <113>β-zone axis of material after quenching with β-phase and diffuse intensity are clearly observed; Right: Key diagram

Several High-Resolution Scanning Transmission Electron Microscopy (HRSTEM) images were taken to enhance understanding of the atomic arrangements. The microscope was aligned with the <110>β-zone axis, hence, showing atomic column arrangements as seen from <110>β. Therefore, any existing α-, α”- or ω-precipitates should be distinguishable from the β-matrix. Figure 34 shows how the atomic motifs seen from <110>β of the β-phase change during the β- to ω-phase transition, which is achieved by a displacive movement of atoms in <111>ω.

![Diagram showing atomic motifs for the β-phase, incompletely transitioned and ideal ω-phase seen from a <110>β-zone axis](image)

Figure 34: Atomic motifs for the β-phase, incompletely transitioned and ideal ω-phase seen from a <110>β-zone axis

As the HRSTEM image on the left of Figure 35 shows, only β-phase is clearly identified with its atomic motifs in the original material condition after quenching. The Fourier filtered image on the right of Figure 35 was obtained by applying a mask to the Fast Fourier Transformation of the HRSTEM image, thus reducing the background noise of the image while increasing the signal from the existing phases. The Fourier filtering confirms that only β-phase is clearly identified. However, comparing the atomic motif in the top left with the one in the bottom right it appears that the atomic positions are somewhat spread in <111>β and less defined then in the bottom right motif. The magnification of atomic columns thus spread, confirms that the longer axis lies in...
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$<111>_{\beta}$. This indicates a localised shift of atomic positions in $<111>_{\beta}$ and thus, provides further evidence for the existence of $\omega_{a}$-nuclei. An atomic displacement along $<111>_{\beta}$ would also explain the background peaks appearing in the neutron diffraction pattern in Figure 30. The presence of these $\omega_{a}$-nuclei is understood to be a very early stage of the $\beta$- to $\omega$-phase transition. Recent work by Zheng et al. (2016a); Zheng et al. (2015) confirms that incompletely transitioned regions show atomic shifts in $<111>_{\beta}$, while a completely transitioned structure will show atomic motifs as seen on the right of Figure 34. The different stages of $\omega$-phase transition are analysed and compared quantitatively within Section 6.3.1.

![Figure 35: Left: HRSTEM image showing $\beta$-matrix with two atomic motifs where atomic positions are slightly shifted towards $\omega$-positions for the top left motif; Right: Fourier filtering of left with same atomic motifs](image)

The observations of the condition of the Ti-1Al-8V-5Fe specimen following quenching from above $\beta$ transus is summarised as follows. The discrete intensity maxima in the neutron and electron diffraction patterns is attributed to the $\beta$-phase, no discrete maxima for $\alpha'$-, $\alpha''$- or $\omega$-phase are seen and atomic arrangements confirm that only $\beta$-phase exists as a stable crystallographic structure. However, diffuse scattering was found for each diffraction method and HRSTEM imaging shows a spread of atomic positions in $<111>_{\beta}$. Therefore diffuse intensity modulations in the diffraction patterns were attributed to a displacive form of short-range ordering of the bcc phase resembling incompletely transitioned $\omega_{a}$-nuclei. The short-range ordering tendency...
of the bcc β-phase is linked to the fact that atoms would diverge from their respective atomic positions within <111>β, which is understood as a precursor of ω-phase transition.

### 6.1.2 Continuous Heating at a Slow Heating Rate to the Final Ageing Temperature

The phase evolution of the Ti-1Al-8V-5Fe alloy during continuous heating to the ageing temperature following a slow heating rate has been recorded. First, the results recorded with high-energy X-rays are presented. These results are then compared in the following two sections 6.1.2.2 and 6.1.2.3 with diffraction data from high-intensity neutron and TEM experiments. It is envisaged that the combination of diffraction techniques will enable determination of the phase transformation sequence and provide insights into the mechanisms of the transition stages.

#### 6.1.2.1 High-Energy X-Ray Diffraction Data during Heating at 5 K/min to 823 K

A detailed description of powder diffraction and the origin of Debye-Scherrer rings was given in Section 4.1. It is understood that in perfect powder diffraction, sets of planes belonging to the same hkl are randomly oriented to the incoming beam, thus diffracting in the form of a circle, which is mapped onto the detector. As the occupation of rings is related to the crystallite size and orientation to the incoming beam, a non-random intensity distribution along the ring either originates from texture or a lack of randomly oriented plane sets due to a small amount of grains within the investigated volume. The radius of the rings is dictated by the crystal structure as it corresponds to the mapping of the scattering vector G_{hkl} for each reflection. The appearance or disappearance of rings is correlated to the appearance or disappearance of a phase.

Figure 36 shows the Debye-Scherrer ring development at a heating rate of 5 K/min to 823 K at representative temperatures. For better comparison of the recorded rings only a sector of each pattern is shown, thereby, enabling the comparison of patterns at four different temperatures. The initial condition at 298 K (bottom left) shows the diffraction pattern after heating the specimen to 1173 K and fast cooling to room temperature. The full rings are shown in the Appendix (Figure 133 to Figure 136).
Simulated patterns showing the locations of Debye-Scherrer rings for each phase and their respective hkl have also been included in the figure.

Diffuse intensity modulations as a function of scattering vector are observed at each temperature, which appear to peak around $Q = 2.74 \text{ Å}^{-1}$ and $Q = 5.09 \text{ Å}^{-1}$. These background peak positions (highlighted in the lower left quadrant) are in close proximity to those detected in neutron diffraction for the as-quenched material in Figure 30. Again, the arguments advanced throughout Section 6.1.1 with respect to diffuse scattering relate to a short-range displacive ordering mechanism of bcc titanium along $\langle 111 \rangle_{\beta}$, which has been shown to exist even at elevated temperatures. (Stassis, Zarestky & Wakabayashi 1978).

![Figure 36: Debye Scherrer ring development over temperature at 5 K/min heating rate; the details shown in the rectangles are discussed further in relation to Figure 38](image)

The lower left quadrant of Figure 36 shows the intensity distribution after fast cooling from above the $\beta$ transus at room temperature. Discrete intensity maxima appear only along rings belonging to $\beta$-reflections. The reason for the inhomogeneous
intensity distribution along β-phase rings lies in the large grain size compared to the small sample size. Thus, at locations where a grain was aligned to the incoming beam in such a way that the Bragg condition was fulfilled, diffraction occurred and intensity was recorded on the detector.

At 643 K the ω-phase has formed, evidenced by a partial occupation of rings on ω-positions. The occupation of β-rings is more prevalent compared to the occupation at room temperature. This is due to local lattice distortions introduced by ω-precipitation. The lattice distortions lead to slight misalignments of β-planes in the local proximity of the ω-precipitate, which increases the likelihood of fulfilling the Bragg condition and thus leads to improved Bragg scattering of the β-phase. The spotty occupation of ω-phase along its rings is explained with nucleation following a strong orientation relationship to the large-grained β-matrix. Thus, the newly formed ω-phase is not randomly oriented but instead, dependent on the β-grain orientation, resulting in a poor occupation of its respective Debye-Scherrer rings. The yellow arrow in this quadrant of

Figure 36 shows the orientation relationship \( \{110\}_\beta \parallel \{110\}_\omega \). A close-up of this part of the pattern is given in Figure 37. The intensity distribution of the ω-phase appears at the same azimuthal angle as the spots of the β-phase, thereby confirming the known orientation relationship between β- and ω-phase.

Figure 37: Magnification of ω-110 and β-110 at 643 K showing their orientation relationship
At 717 K (upper right quadrant in Figure 36) the ω-phase has started to disappear and α”-phase is within the early stages of nucleation. A diffuse cross-shape is highlighted in Figure 36, which is linking two α”-planes (\{112\}_α” and \{022\}_α”) with two other α”-planes (\{200\}_α”, \{130\}_α”) thereby crossing an ω- and a β-plane (\{201\}_ω and \{200\}_β). The development of the intensity distribution within the highlighted rectangle over temperature will be discussed further below with reference to Figure 38. The following α-phase transformation is influenced through the previous processes. In the quarter of the Debye-Scherrer ring taken during holding at 823 K the remainders of another diffuse cross-shape have been highlighted. The α-phase shows higher intensity modulations in the part of the rings that were previously connected through the diffuse streaking.

The intensity development in the rectangular detail (highlighted in Figure 36) of the Debye-Scherrer rings is shown at higher magnification over a temperature range of 652 K to 823 K in Figure 38. This region of interest contains a diffuse cross-shape at ~700 K to ~800 K, but no cross-shape is identified at 652 K, at which temperature a well-developed ω-phase is embedded into the β-matrix. At this temperature the intensity is distributed close to the expected positions of the two phases, with a very strong reflection covering both β-200 and ω-201.

With the decreasing ω-phase fraction and the simultaneous α”-phase nucleation at 702 K, a highly diffuse streaking is observed, which developed from the strong β-200 reflection towards α”-130 and -200 and α”-022 and -112. A similar observation has been reported in a previous study. (Barriobero-Vila et al. 2015a). There are two likely reasons for this observation. One explanation is that the streaking is caused by very thin α”-platelets oriented orthogonally to the streaking direction as shown by Liss et al. (2008a). On the other hand, the streaking could originate from the early stage of the β- to α”-phase transition. The atomic shuffling would be in varying stages, resulting in a continuum of α”-phase lattice parameters due to the increase in dislocation density involved in the β- to α”-phase transformation. (Cheng et al. 2012). An argument in favour of the second hypothesis is that the β-reflection seems to be the origin of the streaking, which would not be the case if the streaking was caused by very fine α”-platelets. At 719 K the ω-phase fraction is significantly reduced and
the α-phase is nucleated, since diffuse intensity maxima are forming at the intersection of the streaks with α-002 and α-102. This observation is more pronounced at higher temperatures as indicated by an arrow. Similar findings were made by Liss et al. (2008b) in a Ti-Al alloy. A possible explanation is that the local lattice strains originating from the β- to α”-phase transformation serve as preferential nucleation sites for the freshly forming α-phase and thereby result in intensity maxima. With an increase in temperature the diffuse cross grows stronger at 734 K, then fades at 778 K and disappears during holding at 823 K. This indicates a correlation between the streaking and the amount of α”-phase as its fraction is highest at 734 K and is mostly transformed into α-phase at 778 K. The phase fraction development will be discussed in more detail with regard to every phase in Section 6.3.2 as part of the Rietveld analysis. Finally, the only features remaining at 823 K are the increased intensity modulations at the previous intersections between α-reflections and the diffuse cross. The role that α”-phase plays within the β- to α-phase transformation can be described as a transitional phase. The α”-phase is more easily formed than the α-phase, because its crystal structure is closer to the β-phase, but is not stable enough so that it will ultimately transform into α-phase. This will be analysed in detail regarding the different crystal structures and resulting lattice strains of formation within Section 6.3.4.

![Figure 38: Intensity distribution over temperature of the diffuse cross-shape marked in the top right of Figure 36.](image)

The following analyses aims to correlate the crystallographic properties of the β- and α”-phases with their orientation relationships in order to explain the likely origin of
the diffuse cross-shape. Figure 39 shows the geometric relations of the β-phase and the α”-phase, which leads to their orientation relationships summarised in Equation (21).

\[
(1\bar{1}0)_\beta \parallel (001)_{\alpha''}
\]

\[
<100>_{\beta} \text{ close to } <100>_{\alpha''}
\]

\[
<110>_{\beta} \text{ close to } <010>_{\alpha''}
\]

Figure 39: Bcc β-phase in the orthorhombic setup of the α”-phase

The drawing on the right of Figure 40 shows that <200>_{\beta} (parallel to \(a_\beta\)) encloses an angle of 45° with <110>_{\beta}, which resembles the angle enclosed by a tangent to β-200 at the position of the reflection and the intensity streaks towards α”-200 and α”-022 (drawing on the left). Following from the geometric relations the atomic motifs for both phases seen from the [011]_β-direction would appear as given on the right of Figure 40. Using the approach by Liss et al. (2006) the angular shift \(\nu\) (highlighted in light blue) of the α”-planes as compared to the β-planes can then be determined from trigonometry (Equation (22)) as 3.994° (lattice parameters at 734 K are \(a_\beta=3.245\ \text{Å}\), \(a_{\alpha''}=2.998\ \text{Å}\), \(b_{\alpha''}=5.055\ \text{Å}\), \(c_{\alpha''}=4.691\ \text{Å}\).
Figure 40: Left: Schematic of diffuse cross and relevant Debye-Scherrer rings, Right: Atomic motifs for α”- and β-phase seen from the [001]_β-direction

\[
\tan(45^\circ + \nu) = \frac{\sqrt{b_{\alpha'}^2 + c_{\alpha'}^2}}{2a_{\alpha'}} \tag{22}
\]

The recorded intensities along each Debye-Scherrer ring were integrated azimuthally and plotted as a function of the scattering vector Q to form a powder diffraction pattern. Rietveld refinements were conducted on these patterns using the software package Maud and resulting patterns are shown in Figure 41 for selected temperatures.
Figure 41: Synchrotron powder diffraction pattern at 298 K, 643 K, 717 K and 823 K

The red pattern at 298 K in Figure 41 shows distinct peaks on β-positions and diffuse scattering in the background, which necessitated the inclusion of background peaks around \( Q = 2.74 \ \text{Å}^{-1} \) and \( Q = 5.09 \ \text{Å}^{-1} \) in order to improve the fitting. The Rietveld fitting resulted in a lattice parameter of the β-phase of \( a_\beta = 3.233 \ \text{Å} \). However, the β-peaks were not ideally fitted. This is most likely a result of the poor grain statistics due to the small sample size, which leads to an inhomogeneous occupation on the Debye-Scherrer rings. Only a small number of the randomly oriented β-grains fulfil the Bragg condition and therefore reduce the occupation of Debye-Scherrer rings. A large, diffracting β-grain possesses a very similar orientation for all planes (hkl) only varying slightly due to lattice defects so that the diffracting intensities cover an increased Q-range compared to smaller grains. In the case of large-grained materials the peak positions may vary slightly and the peak width is increased. This effect has been observed in a similar study of near-β titanium alloys before. (Barriobero-Vila et
al. 2015a). In addition, the peak height will be affected depending on how many grains are oriented in such a way as to the incoming beam to contribute to the respective Bragg peak. This effect is quite significant in the case of β-200 and β-220. Furthermore, very small peaks were found in the pattern, which except for one at $Q = 3.25 \text{ Å}^{-1}$, are all near the α-peak positions listed in Table 7. By comparing the powder diffraction pattern obtained towards the end of the solution treatment at 1173 K with the one obtained following quenching at 298 K (shown in Figure 137 in the Appendix) it appears that the peaks near α-positions are formed during quenching. This information indicates that the quench rate was not high enough to completely suppress the martensitic α’- or α”-transformation in this specific experimental setup. It should also be considered that the sealing of the sample chamber was insufficient at elevated temperatures to completely avoid oxidation of the sample thus, stabilising the α-phase during the subsequent quenching. However, the amount of martensite present in the sample is so small that Rietveld fitting cannot be done with confidence. Hence, the initial α-phase was excluded from the fitting. The outcomes of the Rietveld fitting are presented in Section 6.3.3 and 6.3.4 to firstly analyse the phase fraction development over time and temperature for the different heat treatments and secondly to look at the lattice parameter evolution of the respective phases.

The green pattern at 643 K in Figure 41 shows well-developed ω-phase peaks in addition to the β-phase peaks, and Rietveld fitting revealed phase fractions of 64.6 % β-phase and 35.4 % ω-phase respectively. The lattice parameters were $a_\beta = 3.243 \text{ Å}$, $a_\omega = 4.641 \text{ Å}$ and $c_\omega = 2.848 \text{ Å}$. The previously existing peaks indicative of a martensitic phase are unchanged. The ω-peaks are of low amplitude and broadened, which indicates that the ω-precipitates are small. An approximation of the average precipitate diameter is given through Equation (23). Thus, the diameter D is calculated by the width of an ω-peak at half maximum (FWHM). The FWHM at 643 K of four ω-peaks have been determined and are listed in Table 8. The average FWHM of these peaks equals 0.0337 \text{ Å}^{-1}, hence the approximate precipitate size is 186.7 Å at 643 K.
\[ D = \frac{2\pi}{FWHM} \]  

(23)

Table 8: Measured FWHM of four \(\omega\)-peaks at 643 K

<table>
<thead>
<tr>
<th>Scattering Vector / Å(^{-1})</th>
<th>hkl</th>
<th>FWHM / Å(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.2</td>
<td>001</td>
<td>0.0312</td>
</tr>
<tr>
<td>3.5</td>
<td>111</td>
<td>0.0359</td>
</tr>
<tr>
<td>4.43</td>
<td>002</td>
<td>0.0310</td>
</tr>
<tr>
<td>5.19</td>
<td>301 / 112</td>
<td>0.0365</td>
</tr>
</tbody>
</table>

The blue diffraction pattern at 717 K shows the appearance of peaks on \(\alpha''\)-positions and the disappearance of \(\omega\)-peaks, leading to phase fractions of 79.6 % \(\beta\)-phase, 2.2 % \(\omega\)-phase and 18.3 % \(\alpha''\)-phase. The lattice parameters in this case were \(a_\beta = 3.242\ \text{Å}, \ a_\omega \approx 4.64\ \text{Å}, \ c_\omega \approx 2.85\ \text{Å}, \ a_{\alpha''} = 2.942\ \text{Å}, \ b_{\alpha''} = 5.088\ \text{Å}\) and \(c_{\alpha''} = 4.727\ \text{Å}\). The nucleating \(\alpha''\)-phase has diffuse peaks, which are merging into the background, indicating the presence of extremely fine particles of an anisotropic morphology. This observation is likely due the distribution of \(\alpha''\)-lattice parameters due to the local strain fields originating from the mismatch between nucleating \(\alpha''\)-phase and \(\beta\)-matrix. The previously existing peaks of the martensitic \(\alpha'\)- or \(\alpha''\)-phases have disappeared, including the extra peak that could not be attributed to \(\alpha\)-peak positions.

The pink pattern in Figure 41 from 823 K shows well-developed \(\alpha\)-peaks in addition to the \(\beta\)-peaks. The phase fractions are 64 % \(\beta\)-phase and 36 % \(\alpha\)-phase respectively. The lattice parameters are \(a_\beta = 3.235\ \text{Å}, \ a_\alpha = 2.967\ \text{Å}\) and \(c_\alpha = 4.719\ \text{Å}\). The well-developed peak shape of the \(\alpha\)-phase indicates that the \(\alpha\)-phase is present as well-developed particles of defined shape. Comparing the patterns from 717 K and 823 K reveals that two broad \(\alpha''\)-peaks merge to form a much more defined \(\alpha\)-peak. This is particularly pronounced in the case of \(\alpha''\)-200, \(\alpha''\)-130 and \(\alpha\)-110. The peak development for this example is given in Figure 42 for 717 K to 823 K. Here, two small
but separate $\alpha''$-peaks form a single $\alpha$-peak, proving evidence of the existence of the $\alpha''$-phase as a transitional phase between $\beta$- and $\alpha$-phases.

Figure 42: Peak development of $\alpha''$-200 and -130 to form $\alpha$-110

To evaluate the phase evolution in the Ti-1Al-8V-5Fe alloy during heating to 823 K at a heating rate of 5 K/min, it is instructive to create a Q/time diagram as shown in Figure 43. The azimuthally integrated intensity is shown in colour scale as a function of time and scattering vector Q. On the right-hand side of the graphs the sample temperature is plotted as a function of time on the same time scale. Each horizontal line is understood as a single powder diffraction pattern where the peak-intensity is expressed through the colour scale. Blue corresponds to background intensities, white indicates an increased intensity and red equals the highest intensity level. Therefore, the vertical lines in white and red in the Q/time plot correspond to Bragg Peaks of the phases present. The disappearance or appearance of lines as well as changes in line intensity (colour), are related to phase transformations. The approximate peak positions and their respective hkl-indices in the Q-range of up to 7 Å$^{-1}$ are listed for each phase in Table 7. The change in peak positions, which is particularly pronounced for $\beta$ peaks, is due to a combination of two effects. Firstly, an increase in temperature leads to an increase in lattice parameter and secondly diffusion affects the lattice parameter. As a result of the $\omega$- and $\alpha$-phase
transformations the chemical composition of the phases is altered with a concomitant change in lattice parameters. The changes in lattice parameter caused during and following phase transformations are discussed in more detail in Section 6.3.4.

Figure 43: Q/time diagram during heating at 5 K/min to 823 K, two ω-peaks are indicated by arrows

Figure 43 shows that only β-phase is present as discrete intensity maxima at the beginning of the experiment. Peaks appear at around 570 K on ω-peak positions coinciding with a slight strengthening in intensity of β-peaks. Two examples of separate ω-peaks are indicated by arrows in Figure 43. The magnified detail in Figure 44 shows ω-peaks in an adjusted colour scale in order to improve their visibility. The increase in β-peak intensity with a concomitant onset of a phase transformation was also observed in a β-zirconium alloy by Kabra et al. (2013). The intensity modulations are explained by the release of an extinction effect of almost perfect crystallites through the increasing degree of β-lattice imperfections due to the strains introduced with the phase transformation. The sample was held at high temperatures before the experiment, which led to a β-lattice with very little distortions. Therefore, the incoming synchrotron beam is diffracted less by the β-matrix and the measured β-peaks show a comparatively low intensity. This effect is called primary extinction and it is sensitive to the degree of perfection of the crystal lattice. Thus, the β-peak
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intensity grows stronger when ω-phase is precipitated due to the related distortion of the crystal lattice.

Figure 44: Magnification of the Q-range 3.3 to 4.6 Å⁻¹ between 560 to 823 K

From Figure 44 follows that the disappearance of ω-peaks at roughly 670 K coincides with the appearance of diffuse intensity on α″-peak positions. Thus, indicating the involvement of ω-phase in α″-phase formation. The emerging α″-peaks are very broad with a low intensity amplitude during nucleation and then slowly narrowing while increasing in height when transforming into α-peaks around the same position. As argued before, the diffuse intensity spread on α″-peak positions is most likely due to the fact that the newly-formed α″-precipitates are extremely fine and of anisotropic morphology, and due to the large distribution of α″-lattice parameters caused by local strain fields originating from the mismatch between nucleating α″-phase and β-matrix. At approximately 758 K, the diffuse intensity maxima sharpen, thereby providing evidence of the formation of α-phase from α″-phase.

It should be noted that recent studies by Zheng, Williams and Fraser (2016) have identified an ω″-phase, an ordered orthorhombic structure, to form during slow heating of Ti-5Al-5Mo-5V-3Cr alloy as a precursor of α-phase precipitation. They were able to show that the ω″-phase is formed during heating instead of an α″-phase. The tentative assumption was made that an ordered ω″-phase would form due to Al enrichment in the vicinity of ω-phase precipitates. However, this work on Ti-1Al-8V-5Fe could not identify an ordered orthorhombic structure, but clearly identified the
α”-phase (Section 6.1.2.1). The question that arises is why a usually athermal phase transformation as β to α”-phase can take place at elevated temperatures during slow heating. The short answer identifies the α”-phase as an intermediate, unstable phase, facilitating α-phase precipitation. This point is addressed in detail with regard to necessary lattice strains within Section 6.3.4.1.

In conclusion, the outcomes of the β- to α-phase transformation study from the high-energy X-ray experiment at heating rate of 5 K-min revealed that the phase transformation sequence follows Equation (24).

\[ \beta \rightarrow \beta + \omega \rightarrow \beta + \omega + \alpha'' \rightarrow \beta + \alpha'' \rightarrow \beta + \alpha'' + \alpha \rightarrow \beta + \alpha \]  \hspace{1cm} (24)

The original β-phase consists of randomly oriented, very large grains. The ω-phase consists of small precipitates, which are nucleated following the orientation relationship \( \{110\}_\beta \parallel \{110\}_\omega \). The strong orientation relationship between β- and ω-phase leads to a non-random orientation of ω-particles.

The α”-phase nucleates as extremely fine particles of an anisotropic morphology, leading to the formation of local strain fields due to the mismatch between α”-nuclei and the β-matrix, which results in a large range of α”-lattice parameters.

The α-phase formation is enhanced by the pre-existing α”-phase. It appears that the α”-phase formation serves as an intermediate step in α-phase nucleation. During the α”- to α-phase transformation the precipitates are growing in size and the associated lattice strains between α- and β-phase are reduced, most likely due to the associated change in precipitate shape.

6.1.2.2 High-Intensity Neutron Diffraction Data during Heating at 1 K/min to and Subsequent Holding at 823 K

The proposed phase transformation sequence given in Equation (24) is supported by the neutron diffraction data. The Q/time diagram in Figure 45 shows the diffraction pattern development during heating at a rate of 1 K/min to 823 K. Only β-phase is present at the beginning of the experiment. A low-intensity peak is observed at about 4.62 Å\(^{-1}\) throughout the experiment. This peak originates from the sample environment and is therefore irrelevant to the discussion. From about 500 K on the
β-peaks show small peak shoulders to their left side, which are accompanied by very faint, broad peaks from around 560 K onwards. These new peaks have formed on ω-peak positions and are accompanied by a weakening of β-peak intensity. Hence, indicating different stages of ω-precipitation, which are discussed in more detail with reference to Figure 46. The neutron signal strength for extremely fine precipitates such as the ω-phase is very low compared to high-energy X-ray observations, shown in Section 6.1.2.1. Two examples of very faint ω-peaks are indicated by arrows in Figure 45.

Figure 45: Q/time diagram from neutron diffraction data during heating at a rate of 1 K/min to 823 K, two ω-peaks are indicated by arrows

Another more controversial observation with reference to the synchrotron data is the weakening of β-peaks at the onset of the β- to ω-phase transformation, which is particularly pronounced for β-200 and β-211. This observation is explained through the bigger sample volume in neutron experiments. Due to the larger sample volume the grain statistics remain high enough even in large-grained samples thus, preventing a large effect of primary extinction. Therefore, the effect from lattice imperfections introduced by ω-phase precipitation are negligible compared to the effect a reduced β-phase fraction has on peak height. In contrast, the β-phase signal was strongly affected by primary extinction effects in the case of the synchrotron
data. Hence, the signal grew stronger in that case at the onset of phase transformations.

The disappearance of $\omega$-peaks at roughly 703 K coincides with the appearance of diffuse intensity maxima on $\alpha''$-positions. The $\beta$-peaks lose further intensity at the same time and a significant shift in $\beta$-peak positions is observed. As argued before, these shifts are most probably due to an increase in lattice parameter at increasing temperatures and the enrichment of the $\beta$-phase with the $\beta$-stabilisers V and Fe as a result of their low solubilities in the $\alpha''$-phase. The $\beta$-phase peak heights are reduced, because the $\beta$-phase fraction is reduced due to $\alpha$-phase formation. The concomitant shift in $\beta$-peak positions indicates a change in phase composition due to the redistribution of alloying elements. This change in composition does not only effect peak positions, it also effects the neutron scattering ability of the material and thus the intensity levels of the respective phases. As explained in Section 4.1.1 the neutron scattering ability of a material depends on the sum of the scattering lengths of the elements it contains. Titanium has a negative scattering length while iron has a positive scattering length. Thus, a substitutional enrichment of iron in titanium would result in decreased Bragg scattering in the case of neutron diffraction. As $\alpha$-phase has a low solubility for iron it is expected to form relatively solute lean, which explains the reduced intensity of the $\beta$-phase, while the $\alpha$-phase should have a consequently higher intensity level. The redistribution of alloying elements in early $\alpha$-phase transformation will be analysed quantitatively in Section 6.3.3. At approximately 758 K the diffuse intensity maxima sharpen into a reduced number of peaks thus, indicating the formation of $\alpha$-phase from the $\alpha''$-phase.

As mentioned before the $\beta$-phase starts transitioning into $\omega$-phase from around 500 K on. The powder diffraction pattern evolution is shown in Figure 46. At first the $\beta$-peaks develop peak shoulders to their left side, which transform into double peaks that are accompanied by wide peaks of low amplitude on $\omega$-positions at higher temperatures. These observations indicate that different stages of $\omega$-precipitation exist. The peak shoulders have been identified as an intermediate $\omega$-phase transition in Ti-5Al-5Mo-5V-3Cr alloy by Jones et al. (2009) in a similar heat treatment. This incompletely transformed $\omega$-phase is in a stage of partial $\{222\}$-$\beta$-plane collapse and
therefore not yet of the hexagonal crystal structure. As explained in Section 2.5 once the plane collapse is complete the ideal ω-phase is of hexagonal structure, which is seen by the formation of distinct peaks on ω-positions in the powder diffraction pattern. A possibility to quantify the extent of the β- to ω-phase transition will be discussed in Section 6.3.1.

Figure 46: Neutron powder diffraction pattern at 540 K and 636 K

In conclusion, the neutron diffraction data agrees well with the main findings of the high-energy X-ray diffraction data for a slow heating rate. The main differences are a much stronger loss in β-peak intensity and a significant shift of the β-peak position during the α"-phase precipitation. These observations are explained through a redistribution of alloying elements Fe and V leading to their enrichment in the β-matrix, which will be discussed further in Section 6.3.4.

6.1.2.3 Transmission Electron Microscopy Data during Heating at 5 K/min to 763 K

In general, the electron diffraction data confirmed the findings of the diffraction experiments. In the TEM experiments, two samples were heated at a rate of 5 K/min to 763 K. One sample was aligned to record the changes in the SAD pattern of the <110>β-zone axis and a second sample was used for recording changes in the SAD pattern of the <113>β-zone axis. The SAD pattern sequence in Figure 47 shows the
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diffraction pattern development with an increase in temperature recorded from a zone axis parallel to $<110>_\beta || <110>_{\omega} || <001>_{\alpha''} || <001>_{\alpha}$. The key diagram included in the figure shows the expected positions for the $\beta$- and $\alpha''$-phase as well as positions for two $\omega$- and two $\alpha$-variants, named $\omega_1$ and $\omega_2$ and $\alpha_1$ and $\alpha_2$ respectively.
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Figure 47: SAD patterns recorded from \(<110>_{β}||<110>_{α}>_{ω}||<001>_{α”}>_{ω}||<001>_{α}\) zone axes during heating at a rate of 5K/min. The last pattern was recorded following fast cooling after holding for 6 min at 763 K.

The pattern before heating is basically the same that was discussed for the as-quenched condition in Figure 31. It shows intensity maxima on β-positions and diffuse streaking indicating the presence of nuclei of ωa-phase. The pattern recorded at 553 K is similar to that of the as-quenched condition. The β- to ω-phase transformation temperature was determined as 570 K at a heating rate of 5 K/min in the synchrotron diffraction study (Section 6.1.2.1).

The SAD pattern taken at 668 K shows small changes. The diffuse intensity, indicating directional atomic displacements, resembling nuclei of the ωa-phase is reduced in intensity, it has shifted slightly and shows a faint bow-shape, covering two out of four ω-positions with the α”-position in the centre. This shift in intensity could indicate the disappearance of the ω-phase due to α”-nucleation.

After holding for 2.5 min at 763 K the circular streaking is no longer observed and very weak intensity maxima appeared on ω-positions in addition to diffuse streaking around α”- and α-positions. Also, combined intensity maxima are covering α_{1-120}, α_{2-\bar{2}10}, α”-\bar{2}00 next to β-002. The diffuse intensity distributions indicate that the additional phases are of very small size. In addition, the appearance of extra spots on β-001 and β-111 positions is observed. This observation is explained by atomic displacements in \(<111>_{β}\) leading to a local break of the bcc-symmetry, which allows the appearance of usually forbidden β-111 reflections. In conclusion, it seems that the sample is in a very early stage of (β+ω)- to (β+α”+α)-phase transition.

Finally, the last pattern was recorded after holding the sample for 6 min at 763 K and fast cooling to room temperature. The (β+ω)- to (β+α”+α)-phase transformation was evidently not completed after holding for 6 min at 763 K since the ω-phase has weak but discrete reflections in the pattern. The intensities in the centre of the ω-rectangles are strongest on α”-positions but streaking towards the α-phase positions. In addition, the intensity maxima near β-002 covering α_{1-120}, α_{2-\bar{2}10}, α”-\bar{2}00 have started to split towards their respective α-positions. These observations indicate that the sample was within the early stages of (α”+α)-nucleation when it was cooled to
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room temperature. The observed orientation relationships between $\beta$ and $\omega$-phase are summarised in Equation (25).

$$
\langle 110 \rangle_\beta \parallel \langle 110 \rangle_\omega
$$

$$
[\bar{1}11]_\beta \parallel [001]_{\omega_1}
$$

$$
[\bar{1}1\bar{1}]_\beta \parallel [001]_{\omega_2}
$$

The two dark field images in Figure 48 were taken from the positions marked as g1 and g2 in the SAD pattern in Figure 47 following cooling to room temperature. The dark field image on the left shows relatively small $\omega$-precipitates of approximately 15 to 25 Å in diameter. The dark field image in the middle was taken from a ($\beta+\alpha''+\alpha+\omega$)-position and shows very fine structures embedded into the $\beta$-matrix. These are most likely nuclei of ($\alpha''+\alpha$)-phase within the $\beta$-matrix. The bright field image on the right shows the same fine structures contained in the $\beta$-matrix.

Figure 48: Left: Dark field image of $\omega_1$-position marked as g1 in Figure 47; Middle: Dark field image of $\alpha+\beta+\omega_2$-position marked as g2 in Figure 47; Right: Bright field image of microstructure after cooling.

The SAD pattern sequence in Figure 49 shows the diffraction pattern development of the second sample recorded from a $\langle 113 \rangle_\beta \parallel \langle 101 \rangle_\omega \parallel \langle 702 \rangle_{\alpha''} \parallel \langle 120 \rangle_{\alpha}$-zone axis during heating at a rate of 5 K/min to 763 K. The key diagram shows the positions of the $\beta$-, $\alpha$- and $\alpha''$-phases as well as the positions for two $\omega$-variants.
Figure 49: SAD patterns recorded from \langle113\rangle_\beta \parallel \langle101\rangle_\omega \parallel \langle702\rangle_{\alpha''} \parallel \langle120\rangle_\alpha zone axes during heating at a rate of 5K/min. The last pattern was recorded following fast cooling after holding for 70 min at 763 K.

The pattern before heating is the same shown for the as-quenched condition in Figure 33. Intensity maxima on \beta-positions and elliptical diffuse streaking indicating the
presence of nuclei of ω-phase are observed. The diffuse streaking is weaker in the case of the <113>β-zone axis compared to the <110>β-zone axis. After heating to 553 K the streaking has generally reduced in intensity and the diffuse intensity has shifted towards discrete ω-reflections. Thus, indicating the beginning correlation of atomic displacements in <111>β due to the advancement of the β- to ω-phase transformation. This development is further advanced at 594 K where faint intensity maxima near ω-positions are observed. In addition, diffuse intensity is present at α-2̅10 indicating atomic displacements towards α-formation.

The calculated reflections of the α”-phase in the key diagram may not be the only ones. In the case of the <113>β-zone axis the parallel axis <702>α” is of a high order and hence, not many reflections appear in the simulated pattern. However, the orientation relationship between the α”- and β-phases is not as fixed as for the α- and ω-phases. As detailed in Section 2.4.3.1 Hatt and Rivlin (1968) found that the orientation relationship <100>α” || <100>β and <010>α” || <110>β can deviate by up to 2° and it was this relationship that was used to simulate α”-reflections for the key diagrams. Furthermore, the lattice parameter analysis in Section 6.3.4 will show that the lattice parameters of the α”-phase change significantly in the course of α”-precipitation. Hence, it is reasonable to assume that more α”-reflections should exist in particular in close proximity to α-phase reflections, compared to those given for the α”-phase in the key diagram.

The SAD pattern at 763 K was taken upon reaching the ageing temperature. The diffuse streaking on ω-peak positions has almost disappeared completely whereas the intensity on α-positions has shaped into defined intensity maxima. In addition, some diffuse intensity is present on ½-α”-002 positions, possibly α”-positions, which were not included in the simulation. The intensity maxima near α-2̅10 positions are splitting. For better visibility a magnified image of α-2̅10 is given in Figure 50 in addition to an intensity profile measured along the yellow line, which is confirming the observation. The reason for this observation is most likely the previously explained existence of α”-peaks near α-positions. The synchrotron data discussed in Section 6.1.2.1 showed that the α”- to α-phase transformation starts around 758 K at a heating rate of 5 K/min and is accompanied by the merging of α”-peaks to form α-
peaks on similar positions. Thus, the observed peak splitting at 763 K here, is most likely caused by the starting disappearance of an α”-reflection due to the sharpening of the α-reflection in line with the advancing phase transformation.

Figure 50: Left: Magnification of α-210 at 763 K, Right: Intensity profile along the yellow line

Thus, the observed orientation relationship between the β- and α-phase in the early stages of nucleation and growth can be summarised in Equation (26), which resembles the Burgers orientation relationship seen from a <113>β zone axis.

\[
\begin{align*}
\langle 113 \rangle _{\beta} & \parallel \langle 120 \rangle _{\alpha} \\
[1\bar{1}0]_{\beta} & \parallel [002]_{\alpha}
\end{align*}
\]  

(26)

This sample was cooled to room temperature after a holding time of about 70 min at 763 K. So that the SAD pattern after cooling in Figure 49 shows that the (β+ω)- to (β+α)-phase transformation was completed as no ω-reflections remain. It appears that the α-precipitates are still very fine and thus, diffract with additional spots compared to the key diagram. This observation could also be attributed to an incomplete α”- to α-phase transformation due to the comparatively low ageing temperature.

The dark field image in Figure 51 shows very fine and homogeneously distributed (α+α”)-precipitates of approximately 10 to 20 Å in diameter embedded in the β-matrix. The small size of the precipitates and the homogeneous distribution thereof confirms findings by Zheng et al. (2016b) that an intermediate ω-phase precipitation leads to an improved nucleation of the α-phase. Due to the globular shape of the particles a favoured growth direction could not be determined.
Figure 51: Dark field image of α-precipitates after cooling back to room temperature

The findings of the in-situ TEM study conducted at a heating rate of 5 K/min confirm the transformation sequence determined in the diffraction studies (Sections 6.1.2.1 and 6.1.2.2). The ω-phase is an intermediate phase transition whereas the α”-phase was identified as a precursor to the α-phase transformation. The orientation relationships between β- and ω-phase and β- and α-phase could be confirmed.

An ageing temperature of 763 K appears to be insufficient to stabilise α-phase precipitation if held for only six minutes and some of the ω-phase was retained. However, a holding time of 70 min at 763 K is sufficient to stabilise the α-phase transition and the α-phase formed under these conditions appears to be very fine, of a globular nature and homogeneously distributed with respect to the matrix. This observation provides evidence that the α-phase nucleated at numerous nucleation sites, most probably on finely distributed ω-phase precipitates.

6.1.3 Continuous Heating at a High Heating Rate to the Final Ageing Temperature

The phase evolution of the Ti-1Al-8V-5Fe alloy during continuous heating following a high heating rate to the ageing temperature has been recorded. Results from high-energy X-ray experiments are compared to diffraction data from high-intensity neutron and TEM experiments to determine the phase transformation sequence and provide insights into the respective transformation mechanisms. There are distinct differences between the observations made at the higher heating rates as will be outlined below.
6.1.3.1 High-Energy X-Ray Diffraction Data recorded during Heating at 100 K/min to 823 K

Figure 52 shows the Debye-Scherrer ring development at a heating rate of 100 K/min to 823 K with ring quarters shown at the same temperatures as in Figure 36. The full ring patterns are given in the Appendix (Figure 138 to Figure 141).

Figure 52: Debye Scherrer ring development over temperature at 100 K/min heating rate

The diffuse intensity modulations with maxima around $Q = 2.74 \text{ Å}^{-1}$ and $Q = 5.09 \text{ Å}^{-1}$ are observed throughout the experiment (as was the case for a 5 K/min heating rate). Thus, confirming the assumption that this phenomenon is caused by the directional atomic displacements along $<111>\beta$ and not by differences in heat treatments. The $\beta$-phase is the only phase with intensity maxima on its respective rings (though poorly occupied) from room temperature up to the ageing temperature at 823 K. Intensity along rings on $\omega$-positions was not observed at any temperature. This observation indicates that the $\beta$- to $\omega$-phase transition is at least partially time dependent, which would not be the case for a completely martensitic type of phase transformation.
Hence, the β- to ω-phase transition is not solely achieved by atomic shuffling, (which would be expected to be independent of the heating rate), but also has a diffusional component (most likely a redistribution of alloying elements), which can be suppressed by a sufficiently high heating rate. These findings are in agreement to the conclusions of Nag et al. (2011) and Devaraj et al. (2012) who studied Ti-Mo near-β alloys and identified a dependency of the extent of atomic displacements in \( <111> \) on preliminary redistribution of Mo. They found that a local depletion of Mo was required to achieve a full β- to ideal ω-phase transition.

The ring sector at 823 K was taken after holding for 31 s. It shows very early \( \alpha'' \)-nucleation. Two faint diffuse cross-shapes appeared during holding at 823 K, which are shown in the magnification in Figure 53. They are of similar appearance to the one identified as nucleating \( \alpha'' \)-phase in Figure 36 at 717 K. Hence, a significant delay of more than 100 K is observed for the start of the β- to \( \alpha'' \)-phase transformation. The slower \( \alpha'' \)-phase nucleation kinetics are caused by the combined effects of the reduced number of nucleation spots due to the lack of an intermediate ω-phase transition and the lack of diffusion caused by the higher heating rates, (which is required to enable the redistribution of β-stabilisers and hence stabilise the \( \alpha'' \)-phase).

![Figure 53: Magnification of two faint diffuse cross-shapes at 823 K](image)

The recorded intensities along each Debye-Scherrer ring were integrated azimuthally and plotted as a function of the scattering vector \( Q \) to form the powder diffraction patterns shown in Figure 54 for selected temperatures. They remain very close to the pure β-phase pattern at 298 K and no intensity maxima on ω-peak positions were observed at any temperature. Only the powder diffraction pattern gathered after
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holding for 31 s at 823 K shows slight variations. It confirms the previous statement that α”-phase precipitation is in a very early stage as α”-peaks are very broad and hence, indicating small, possibly anisotropically shaped nuclei. In the case of α-102 at about 3.6 Å⁻¹ peak splitting is observed, which is confirming that at this moment the dominant phase present should be α”-phase and not α-phase.

Figure 54: Powder diffraction patterns during heating at a rate of 100 K/min to 823 K.

The pattern development is summarised in the Q/time diagram in Figure 55. The distinct intensity maxima at β-phase positions confirm that β-phase is present throughout the experiment. Very faint peaks exist near α-positions, but they did not have a significant effect on the pattern analysis and hence were disregarded in the further analyses. At no time during the heat treatment were intensity maxima found on ω-positions.
The $\omega$-phase does not seem to play a role in the precipitation of $\alpha''$-phase at a heating rate of 100 K/min in this alloy.

### 6.1.3.2 High-Intensity Neutron Diffraction Data during Heating at 20 K/min to and Subsequent Holding at 823 K

The absence of an intermediate $\beta$- to ideal $\omega$-phase transformation during heating to the holding temperature at a fast heating rate is confirmed by the neutron diffraction data. The Q/time diagram in Figure 56 shows the diffraction pattern development during heating at a rate of 20 K/min to 823 K and subsequent holding at the ageing temperature. A low-intensity peak is observed at about 4.62 Å$^{-1}$ throughout the experiment, which is stemming from the sample environment and was therefore disregarded in the analysis. Only $\beta$-phase is present at the beginning of the experiments and there are no distinct intensity maxima on $\omega$-phase positions. However, $\beta$-peak shoulders as described with reference to Figure 46 are observed from about 530 K on, indicating an incomplete $\beta$- to $\omega$-phase transition. The $\alpha''$-phase nucleation is delayed to approximately 721 K at this heating rate. The $\alpha''$-peak sharpening indicates that the $\alpha''$- to $\alpha$-phase transformation is finished around 805 K. The nucleation of the $\alpha''$-phase coincides with a strong reduction in $\beta$-peak intensity and a significant shift of the $\beta$-peak positions in similar vein to the observations for the neutron diffraction data at a slow heating rate (see Section 6.1.2.2). The loss of $\beta$-peak intensity is mainly caused by the reduction of the $\beta$-phase fraction but the $\beta$-stabiliser enrichment of the $\beta$-phase cannot be discounted. The enrichment in solute...
of the β-phase leads to a shift of β-peak positions due to its effect on $a_\beta$, which will be analysed and discussed as part of Section 6.3.4.

Figure 56: Q/time diagram during heating at a rate of 20 K/min to 823 K

In conclusion, the diffraction data from neutron experiments indicate that the phase transformation sequence alters at different heating rates and a heating rate of 20 K/min leads to the transformation sequence in Equation (27).

$$\beta \rightarrow \beta + \omega_{inc} \rightarrow \beta + \alpha'' \rightarrow \beta + \alpha'' + \alpha \rightarrow \beta + \alpha$$ (27)

Independent of the heating rate a strong loss in β-peak intensity was observed simultaneously to the β- to α”-phase transformation for both neutron diffraction experiments. The main cause of the loss in β-peak intensity lies in the reduced β-phase fraction due to the α”-phase transition. The secondary cause lies in the enrichment of the β-matrix with Fe leading to a reduced diffraction signal. The strong β-peak position shift also indicates an enrichment of Fe and V in the β-matrix. These correlations will be analysed quantitatively in Section 6.3.3 and 6.3.4.

6.1.3.3 Transmission Electron Microscopy Data during Heating at 20 K/min to 763 K

The electron diffraction data generally confirm results from the diffraction experiments. The sample was heated at a heating rate of 20 K/min to 763 K. The SAD pattern sequence in Figure 57 shows the diffraction pattern development for a zone
axis parallel to $<110>_{\beta} \parallel <110>_{\omega} \parallel <001>_{\alpha''} \parallel <001>_{\alpha}$ over temperature. As before, a key diagram is also included.

Figure 57: SAD patterns recorded from $<110>_{\beta} \parallel <110>_{\omega} \parallel <001>_{\alpha''} \parallel <001>_{\alpha}$ zone axes during heating at a rate of 20 K/min. The last pattern was recorded following fast cooling after holding for 10 min at 763 K
The diffuse streaking at room temperature indicating \( \omega \)-nuclei has shifted significantly after heating to 533 K. It shifted away from \( \omega \)-phase positions and closer to \( \alpha'' \)- and \( \alpha \)-phase positions. In addition to the previously present \( \beta \)-reflections, weak intensity maxima have developed on \( \alpha'' \)-positions. The orientation relationship between \( \beta \)- and \( \alpha'' \)-phase is summarised in Equation (9). A study by Barriobero-Vila et al. (2015a) also found that \( \alpha'' \)-phase is an intermediate step to the \( \alpha \)-phase transformation in heat treatments with higher heating rates, which inhibit intermediate \( \omega \)-phase precipitation. However, the detected intensity maxima on the \( \alpha'' \)-positions are very small compared to \( \beta \)-reflections, thus indicating that the phase fraction of \( \alpha'' \)-phase is very small. Hence this observation explains why \( \alpha'' \)-phase was not detected during the neutron diffraction experiments at the same heating rate.

\[
\begin{align*}
\langle 110 \rangle_\beta & \parallel \langle 001 \rangle_\alpha'' \\
[1\overline{1}0]_\beta & \parallel [010]_\alpha'' \\
(002)_\beta & \parallel (\overline{2}00)_\alpha'' 
\end{align*}
\]

The pattern taken at 679 K shows that intensity maxima on \( \alpha'' \)-reflections became more diffuse again but remain in close proximity to \( \alpha'' \)- and \( \alpha \)-phase positions. The diffuse intensity spread around \( \alpha'' \)-phase reflections are an indicator of the on-setting \( \alpha'' \)-phase transformation. Due to the higher heating rate a complete \( \omega \)-phase transformation was suppressed, thus the \( \beta \)-phase is retained to higher temperatures but contains incompletely transitioned \( \omega \)-precipitates. With increasing temperature both the incompletely transitioned \( \omega \)-phase and the \( \beta \)-phase are destabilising due to the on-setting \( \alpha'' \)-phase transition. Hence, some atoms are shifting to lattice positions of the \( \alpha'' \)-phase. The local ordering of atoms to form \( \alpha'' \)-phase nuclei is indicated by the diffuse intensity maxima. In addition, very faint intensity maxima on \( \beta \)-001 and \( \beta \)-111 positions are observed, which are indicating the appearance of forbidden \( \beta \)-reflections due to a local loss of bcc symmetry.

After holding for about one minute at 763 K the diffuse streaking has almost disappeared and definite intensity maxima are covering \( \alpha'' \)-positions as well as positions for both \( \alpha \)-variants. The extra-spots indicating forbidden \( \beta \)-reflections are still weak, but more defined. The disappearance of the diffuse lattice streaking
indicates the stabilisation of the β-lattice due to the precipitation of α’’- and α-phases. Both α-variants exist and have nucleated with the Burgers orientation relationship given in Equation (29).

\[
\langle 110 \rangle _\beta ||\langle 001 \rangle _\alpha \\
\langle 001 \rangle _\beta ||\langle 110 \rangle _{\alpha 1} \\
\langle 001 \rangle _\beta ||\langle 110 \rangle _{\alpha 2} \quad (29)
\]

The last SAD-pattern in Figure 57 was taken after cooling to room temperature. The sample was held at 763 K for approximately 10 min. It shows two types of streaking and the continued existence of forbidden β-reflections. The first type of streaking is cross- and bow-shaped diffuse streaking between β-positions. Here, the diffuse intensity is covering positions of the α’’-phase and both α-variant positions while avoiding ω-positions at the end of the cross. The contrast in the magnified image on the left of Figure 58 has been modified to highlight these diffuse features. The diffuse streaking is similar to the features discussed with reference to the Debye-Scherrer rings (Figure 38). The shapes are indicators for a continuous distribution of lattice parameters from β- to (α’’+α)-phase due to local strain fields around very fine (α’’+α)-particles. Furthermore, intensity maxima are seen on α’’-positions near β-positions, which are streaking into α-positions at both sides. This indicates an early stage of the α’’- to α-phase transition. A third type of streaking is more visible in the magnified detail to the right of Figure 58. It overlaps with β-reflections and is marked in yellow. The streaking appears to originate from positions of the α_1-120 and α_2-210 type and is crossing through β-002 type positions. The diffuse intensity distribution as well as the directional streaking are indicators of very fine, anisotropically shaped (α’’+α)-particles such as platelets where the thinnest dimension of the plate lies perpendicular to the streaking direction.
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Figure 58: Left and Right: Magnified images showing the same detail of the last SAD pattern in Figure 57 with modified contrast to highlight different types of diffuse streaking; Middle: Key diagram

The existence of these fine (α”+α)-platelets is proven through the bright field image in Figure 59, which was taken after cooling to room temperature. The microstructure is of the basket weave type where very fine (α”+α)-laths of approximately 50 Å thickness are embedded in the β-matrix. The small size of the (α”+α)-precipitates provides evidence of the observed diffuse nature of the diffraction spots in the previously shown SAD patterns. This basket weave structure could be a transition microstructure preceding the completed α”- to α-phase transformation.

Figure 59: Bright field image of (α”+α)-laths embedded in the β-matrix

The fact that discrete α”-phase diffraction spots appear in the SAD diffraction patterns instead of diffuse streaking near ω-positions, provides evidence that an ideal ωiso-phase does not form at higher heating rates in this alloy. Thus, indicating that the full β- to ω-phase transformation includes a diffusional component, which is inhibited by a fast heating rate. Instead α”-phase was found as an intermediate phase. The
reason that $\alpha''$-phase was not found in the neutron diffraction study might be attributed to the small amount of $\alpha''$-phase present, indicated by the weakness of its reflection. Also, $\alpha''$-phase existed for a very short time only as faint, but defined reflections before it was replaced by diffuse streaking arguably caused by anisotropical lattice vibrations of the $\beta$-phase in directions supporting the approaching $\alpha$-phase transition. In the case of the synchrotron experiment the heating rate was significantly higher (100 K/min) and hence, possibly inhibiting a low-temperature $\beta$- to $\alpha''$-phase transformation.

A holding time of 10 min at 763 K before fast cooling was sufficient to stabilise the $(\alpha''+\alpha)$-phase so that a basket weave type microstructure with very fine $(\alpha''+\alpha)$-laths embedded in the $\beta$-matrix formed.

6.1.4 Fast Heating Rate with an Intermediate Holding at 623 K before Heating to the Final Ageing Temperature

Neutron diffraction data collected during heating at a rate of 20 K/min to an intermediate holding step at 623 K for 70 min, followed by holding at 823 K is detailed in this Section. The mechanism of the phase transformation in this instance was similar to that observed at lower heating rates (Section 6.1.2).

The Q/time diagram in Figure 60 shows the diffraction pattern development during heating at a rate of 20 K/min to 623 K, holding for 70 min and then continuing heating at the same rate to and subsequent holding at 823 K. The alignment between instrument, detector and sample environment was less optimal in this case as compared to previously detailed neutron diffraction experiments, leading to the appearance of four peaks with varying intensities at about 2.66 Å$^{-1}$, 2.82 Å$^{-1}$, 4.0 Å$^{-1}$ and 4.68 Å$^{-1}$ throughout the experiment. These peaks are originating from the sample environment, as explained in Section 6.1.2.2.
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Figure 60: Q/time diagram during heating at a rate of 20 K/min to isothermal holding for 70 min at 623 K and continued heating to 823 K, two ω-peaks are indicated by arrows

Only β-phase is present at the beginning of the experiments. As discussed with reference to Figure 46, β-peak shoulders are formed during heating from about 530 K on, indicating the beginning β- to ω-phase transition. After holding for about 109 s at 623 K, diffuse peaks appear on ω-peak positions coinciding with a slight weakening in intensity of β-peaks and also a shift in β-peak positions. Two examples of separate ω-peaks are indicated by arrows in Figure 60. The shift in position is more easily observed in the case of β-200 and β-211 as the peak-overlapping between β- and ω-peaks is reduced with increase in Q. The detail in Figure 61 shows these β-peaks in the relevant time scale with adjusted colour scale to improve the visibility of ω-peaks. The observed β-peak shift might be due to the enrichment of the β-matrix with Fe and V resulting from the diffusion of alloying elements away from the precipitated ω-phase. Such enrichment of alloying elements in the β-phase would lead to a decrease of the β-lattice parameter and thus to a shift of β-peaks to higher Q-values. Alternatively lattice strains created through the precipitation of ω-phase could also affect the lattice parameter. The sometimes concurrent influence of temperature changes, diffusion and lattice strains on the lattice parameters of the respective phases will be discussed in more detail in Section 6.3.4.
Figure 61: Magnification of the Q-range 3.8 to 4.8 Å\(^{-1}\) during heating to and holding for 30 min at 623 K

After holding for 70 min at 623 K, heating was continued to 823 K. At about 685 K the ω-peaks disappear, coinciding with a slight increase in β-peak intensity and also the formation of diffuse intensity maxima on α”-peak positions. Figure 62 shows a magnification of the relevant Q-range with adjusted contrast, highlighting the diffuse intensity spread of initial α”-peaks and the intensity increase of β-211 (marked with the right arrow) in the early stages of the β- to α”-phase transition. The increase in β-peak intensity indicates that some of the ω-phase transforms back into β-phase before the transition continues to α”-phase. Furthermore, even though ω-102, -211 and -300 lie in close proximity to α”-113 and -023 positions a gap due to reduced amplitude of intensities is observed (black bracket) while at the same time a streaking connects the α”-positions with β-211 (left arrow). This indicates a continuum of lattice parameters between α”- and β-phase originating in the lattice strains induced in that phase transformation. Figure 62 shows that subsequently, the intensity maxima on α”-peak positions sharpen and gain in intensity while β-peaks loose intensity and return to similar levels to those during isothermal holding at 623 K. Simultaneously, another shift in the β-peak position is observed. Thus, indicating a second redistribution of alloying elements, this time between the β- and α”-phases. As argued earlier the peak width of the emerging α”-peaks indicates firstly that the new-formed α”-precipitates are extremely fine particles of an anisotropic morphology and secondly a continuous distribution of α”-lattice parameters due to
local strain fields originating from the mismatch between the nucleating $\alpha''$-phase and the $\beta$-matrix exist. At approximately 816 K the diffuse intensity maxima on $\alpha''$-positions sharpen, thus indicating the formation of $\alpha$-phase from the $\alpha''$-phase.

Figure 62: Magnification of the Q-range 4.1 to 4.8 Å$^{-1}$ during holding for 15 min at 623 K, heating to and holding for 5 min at 823 K

In conclusion, the neutron diffraction data following a fast heating rate with an isothermal holding step at $\omega$-precipitation temperatures indicate that the phase transformation sequence follows the same sequence as in the case of the slow heating rate given in Equation (24). Thus confirming that the $\beta$- to ideal $\omega_{iso}$-phase transformation has a diffusional component, which is enabled at a low heating rate or an isothermal holding step at the $\omega$-precipitation temperature near 623 K. These results confirm assumptions by Ivasishin et al. (2005) that the ageing response of near-$\beta$ titanium alloys upon slow heating could be simulated through an intermediate holding at $\omega$-precipitation temperatures, followed by subsequent heating to $\alpha$-phase transformation temperature.

6.1.5 Conclusions from the In-Situ Diffraction Studies

The findings of the in-situ diffraction studies show that the heating rate affects the phase transformation sequence. The sequence followed at a rate of 20 K/min or higher is shown in Equation (27). The $\beta$-phase transforms directly into the $\alpha''$- and
then into the $\alpha$-phase. By contrast, both a heating rate of maximal 5 K/min to the ageing temperature and heating at a rate of 20 K/min with isothermal holding at the $\omega$-precipitation temperature of 623 K follow the transformation sequence given in Equation (24). Hence, precipitation of ideal $\omega$-phase occurs before $\alpha''$- and $\alpha$-phases are formed. These observations provide convincing experimental evidence that the ideal $\omega$-phase only forms at a sufficiently low heating rate or during holding in the correct temperature range. This time dependence of the phase transformation suggests that the mechanism of the $\beta$- to $\omega$- transformation is at least partially diffusion controlled. The $\omega$-phase disappears upon precipitation of $\alpha''$-phase, which suggests that $\alpha''$-phase can nucleate inside the $\omega$-phase or on the $\omega/\beta$-phase boundary and then grow while dissolving the $\omega$-precipitate, following the direct $\omega$- to $\alpha''$-phase transformation path given by Equation (30). However, at high heating rates including an isothermal holding step at $\omega$-precipitation temperatures, the $\beta$-peak intensity increases for a short time while the $\omega$-phase decomposes and $\alpha''$-phase is precipitating, thus indicating that $\omega$-phase transforms into $\beta$-phase first and then into $\alpha''$-phase, following the transformation sequence in Equation (31). The following sections will help to clarify these observations.

\[
\omega \rightarrow \alpha'' \quad \text{(30)}
\]

\[
\omega \rightarrow \beta \rightarrow \alpha'' \quad \text{(31)}
\]

The $\beta$-phase shows directional atomic displacements in the $<111>_\beta$ directions during heating at any rate from room temperature to elevated temperatures causing diffuse intensities in the diffraction patterns. In the neutron and synchrotron studies these diffuse intensities manifested in background peaks close to close-packed lattice directions, caused by anisotropical lattice vibrations in these directions. In the case of the SAD patterns lattice streaking was at different positions for the varying heating rates, indicating varying types of directional atomic displacements, which represent a precursor to the respective type of phase transition.
6.2  Ex-Situ High-Resolution Scanning Transmission Electron Microscopy Studies

The ex-situ STEM studies were designed to clarify the β- to α-phase transformation at the atomic scale with regard to microstructural development, growth directions and alloying element distributions. Four different heat treatments were designed to determine the influence of heating rates and isothermal holding at temperatures near ω-precipitation. Continuous heating was done at rates of 1 K/min, 20 K/min and 100 K/min to 823 K. One heat treatment was done at a heating rate of 100 K/min to 823 K including initial isothermal holding for one hour at 623 K.

6.2.1  Fast Cooling from 593 K

This temperature was selected to investigate the early stages of ω-phase precipitation. A sample was heated continuously at 1 K/min to 593 K and then fast cooled to room temperature. The neutron diffraction data presented in Section 6.1.2.2 showed that nucleation of ω-phase starts at 553 K so that the ω-phase would be expected to exist as well-developed particles at 593 K. The bright field image in Figure 63 shows homogeneously distributed, fine ω-precipitates in a β-matrix.

![Figure 63: Bright field image of fine ω-precipitates in a β-matrix after heating by 1 K/min to 593 K and fast cooling to room temperature](image)

The SAD patterns form the same sample are shown in Figure 64 and Figure 65 from the \(\langle 110\rangle_\beta || \langle 110\rangle_\omega\) and the \(\langle 113\rangle_\beta || \langle 101\rangle_\omega\)-zone axis respectively. Both confirm the existence of well-developed ω-precipitates. Thus, the β- to ω-phase
transformation is completed and the isothermal ω-phase (ω_{iso}) has a hexagonal structure with an orientation relationship to the β-phase as given in Equation (25).

Figure 64: Left: SAD pattern of <110>β-zone after heating at 1 K/min to 593 K and fast cooling to room temperature; Right: Key diagram

Figure 65: Left: SAD pattern of <113>β-zone after heating at 1 K/min to 593 K and fast cooling to room temperature; Right: Key diagram

The dark field images in Figure 66 were taken from ω-positions of both variants marked as g1 and g2 in Figure 64. The images show homogeneously distributed ω_{iso}-precipitates of varying sizes up to ~50 Å in diameter.
Results and Discussion

Figure 66: Left: Dark field image of $\omega_2$-position marked as g1 in Figure 64; Right: Higher magnification dark field image of $\omega_1$-position marked as g2 in Figure 64

The High-Resolution Scanning Transmission Electron Microscopy (HRSTEM) image on the left of Figure 67 shows four well-developed $\omega_{iso}$-precipitates of two different $\omega$-variants formed during heating to 593 K. By applying Fourier filtering to the HRSTEM image, the high frequency noise is reduced while increasing the signal from $\beta$- and $\omega$-phase (right of Figure 67). The white rectangle in the HRSTEM image marks the region shown in the Fourier filtered image at higher magnification. This image shows atomic motifs of both $\omega$-variants and the $\beta$-matrix. Atomic mismatches of 0.6° to 1° between $<001>_{\omega}$ and $<111>_{\beta}$ for both $\omega$-variants, indicate the presence of lattice strains resulting from $\omega$-precipitation. Banerjee, Tewari and Dey (2006) have shown in earlier research that the interference of $\omega$-precipitates of two different variants in close proximity can lead to the observed mismatches, which would not be expected for $\omega$-precipitates from the same variant.
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Figure 67: Left: HRSTEM image showing four $\omega_{iso}$-precipitates in the $\beta$-matrix of two different variants; Right: Fourier filtering of left with atomic motifs for both $\omega$-variants and the $\beta$-phase.

Energy-Dispersive X-Ray Spectroscopy (EDS) was performed to assess compositional variations in the sample. Compositional maps are shown in Figure 68 in addition to a STEM image of the area of interest. The compositional maps are overlayed with the STEM image to highlight the interrelation of structural features and composition. The bar in the STEM image marks the position of the linescan shown in Figure 69. The STEM image shows different shades of grey. Darker grey indicates lower concentrations of heavy elements (V and Fe) and vice versa. Compositional variations exist on a scale smaller than 10 Å and thus, significantly smaller than the $\omega$-precipitates, which were found to be up to $\sim$50 Å in size. The statistical error of the measurement are of the order as the variations and thus, no quantitative conclusion on compositional differences between matrix and $\omega$-precipitates can be made.
Results and Discussion

Figure 68: EDS composition maps of the alloying elements overlayed with the STEM image of the area of interest shown in grey

Figure 69: Results of the linescan marked in the STEM image in Figure 68

In conclusion, heating at 1 K/min to 593 K produces homogenously distributed, well-developed \( \omega \)-precipitates up to \(~50 \text{ Å}\) in diameter of somewhat undefined shape. Multiple variants have the same orientation relationship with the \( \beta \)-matrix. Atomic mismatches below 1° were found between \{001\}_\omega \) and \{111\}_\beta \) for \( \omega \)-precipitates of different variants indicating that lattice strains result from \( \omega \)-precipitation. Compositional variations are observed in STEM images but could not be quantified
Results and Discussion

reliably as the statistical error of the EDS-measurement is close to the magnitude of the variations.

6.2.2 Fast Cooling from 653 K

At 653 K the ω-transition is completed at a heating rate of 1 K/min and hence, the observations described in the previous Section 6.2.1 can be compared to early ω-precipitation found at 593 K. Furthermore, samples heated at 20 K/min and 100 K/min to 653 K show an incomplete stage of ω-transition. Observations for the higher heating rates show that elemental partitioning is reduced and therefore the β- to ω-phase transition is hindered, resulting in an incompletely transitioned ω<sub>inc</sub>-phase.

The dark field image on the left of Figure 70 shows homogeneously distributed, fine ω-precipitates in the β-matrix, taken from a sample heated at 1 K/min to 653 K followed by fast cooling to room temperature. The bright field image of the sample heated at 20 K/min, on the right of Figure 70, shows only the β-matrix. If ω-precipitates would exist they would either be of such a small size that they cannot be captured at this magnification or in a state of incomplete transition (ω<sub>inc</sub>-phase), thus not leading to a significant diffraction contrast in the image.

Figure 70: Dark and bright field images after heating to 653 K and fast cooling to room temperature: Left: β-matrix with small ω-precipitates (1 K/min); Right: β-matrix (20 K/min)
The SAD patterns in Figure 71 emphasise the varying states of ω-phase for the respective heating rates. The SAD pattern in the top left (1 K/min) shows that β- and ω-phase exist as discrete intensity maxima. In contrast, patterns for the higher heating rates in the bottom left (20 K/min) and (100 K/min) show diffuse streaking of circular shape similar to the appearance of the SAD pattern before heating shown in Figure 31. In both cases the diffuse streaking lost intensity in proximity to β-positions, the streaking does not describe a full circle and very faint intensity maxima have formed on ω-positions. This observation indicates that the ω-phase transition began but is in a stage of incomplete transition.

Figure 71: SAD patterns of <110>β-zone after heating to 653 K and fast cooling to room temperature and key diagram

The dark field images in Figure 72 provide insights into the different stages of the β-to ω-phase transition as a function of heating rate. The dark field images at the top were taken from both ω-variants marked as g1 and g2 in the top left of Figure 71 for a 1 K/min heating rate. The ω-precipitates have grown to diameters of 70 to 110 Å and are still homogeneously distributed throughout the β-matrix. Compared to precipitates formed during heating to 593 K the morphology appears more defined
and is best described as globular. The $\omega$-precipitate size of 186.7 Å determined from the synchrotron data for a heating rate of 5 K/min at 643 K in Section 6.1.2.1 is of a comparable magnitude to the TEM observations.

The dark field images at the bottom show incompletely transitioned $\omega_{inc}$-precipitates in the $\beta$-matrix. The left image was taken from the $\omega_1$-position marked in the bottom left of Figure 71 for a heating rate of 20 K/min. The right image was taken from a distinct $\omega_2$-position as marked in the bottom right of Figure 71 for a heating rate of 100 K/min. The image on the bottom left shows a high density of small, homogeneously distributed $\omega_{inc}$-precipitates with diameters of up to 30 Å. The image on the bottom right shows a smaller amount of larger $\omega_{inc}$-precipitates with diameters between 30 to 50 Å. Other dark field images of the samples that are not shown confirm that the density of $\omega_{inc}$-precipitates is higher for the lower heating rate but that they are smaller in their dimensions. These results indicate that the initial growth of $\omega_a$-nuclei is enabled to a wide extent for a heating rate of 20 K/min while the continuation of the $\omega$-transformation is suppressed most likely due to a lack of diffusion that is required to achieve this step. Thus, leading to a homogeneous distribution and high density of small $\omega_{inc}$-precipitates in the matrix. With a further increase in heating rate to 100 K/min the initial growth of $\omega_a$-nuclei is also hindered, leading to a lower density of slightly larger $\omega_{inc}$-precipitates. The following analysis will follow up on these observations by comparing the state of the $\beta$- to $\omega$-phase transition at the atomic level and the distribution of alloying elements in the respective phases in order to investigate the impact of diffusion on the $\beta$- to $\omega$-phase transformation in the Ti-1Al-8V-5Fe alloy.
Figure 72: Dark field images of ω-positions marked in the respective SAD pattern in Figure 71: Top Left: ω2-position marked as g1 (1 K/min); Top Right: ω1-position marked as g2 (1 K/min); Bottom Left: ω1-position marked with small circle (20 K/min); Bottom Right: ω2-position marked with small circle (100 K/min)

The HRSTEM image to the left in Figure 73 shows two large ωiso-precipitates of the same ω-variant that formed during slow heating to 653 K (1 K/min). The white rectangle marks the region shown in the Fourier filtered image detail with a higher magnification on the right. The Fourier filtering shows the atomic motifs for ω-precipitates compared to the β-matrix. The two ω-precipitates observed after cooling from 653 K are larger and of the same variant in contrast to those found after cooling from 593 K. The mismatch of 0.6° to 1° found between <001>ω and <111>β for ω-precipitates after cooling from 593 K cannot be observed for ω-precipitates of the
same variant. This indicates that the origin of the mismatch was lying in the necessity of the system to integrate two different variants in close proximity into the $\beta$-matrix.

![HRSTEM image](image)

**Figure 73**: Left: HRSTEM image showing two $\omega_{iso}$-precipitates of the same variant in the $\beta$-matrix; Right: Magnified Fourier filtering of left with atomic motifs for both $\omega$-precipitates and the $\beta$-matrix (1 K/min)

The recorded HRSTEM images for the fast heating rates show mainly $\beta$-phase. However, it was possible to record a large $\omega_{inc}$-precipitate embedded in the $\beta$-matrix for the sample heated by 100 K/min (shown in Figure 74). The atomic motifs in the magnified Fourier filtering on the right display the early stage of the $\beta$- to $\omega$-phase transition. The plane collapse of the $(111)_\beta$-planes is incomplete, which is seen due to the missing alignment of atoms along $<110>\omega$ and $<112>\beta$ respectively.
Figure 74: Left: HRSTEM image showing an $\omega_a$-nucleus in the $\beta$-matrix; Right: Fourier filtering of left with atomic motifs for the $\omega_a$-nucleus and the $\beta$-phase (100 K/min)

The EDS-analysis led to the compositional maps shown in Figure 75 (1 K/min) and Figure 77 (20 K/min) followed by the results of their respective linescans in Figure 76 and Figure 78. The compositional variations of the sample heated at 1 K/min to 653 K have slightly increased in magnitude as compared to the condition heated to 593 K. Also the STEM image shows colour variations on a larger scale than before. This is a clear indicator that the growth of $\omega$-precipitates is accomplished at least partially by diffusion. However, the elemental concentration variations picked up by the technique are still significantly smaller than the $\omega$-precipitates. Also the STEM image on the left of Figure 75 does not allow an optical separation of $\omega$-precipitates and matrix thus, further increasing the difficulty of drawing conclusions based on these results. Nevertheless, when directly comparing the results for the fast heating rate with the slow heating rate it appears that the extent of compositional variations are significantly higher in the slowly heated sample. This indicates a correlation between heating rate, diffusion and the magnitude of the $\beta$- to $\omega$-phase transition. The effect of heating rate on element diffusivities and the magnitude of the $\beta$- to $\omega$-phase transformation will be analysed in more depth within Section 6.3.1 and 6.3.4.
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Figure 75: EDS composition maps of the alloying elements overlayed with the STEM image of the area of interest shown in grey (1 K/min)

Figure 76: Results of the linescan marked in the STEM image in Figure 75 (1 K/min)
Figure 77: EDS composition maps of the alloying elements overlayed with the STEM image of the area of interest shown in grey (20 K/min)

Figure 78: Results of the linescan marked in the STEM image in Figure 77 (20 K/min)

The observations of the sample heated at 1 K/min to 653 K and fast cooled to room temperature indicate that the growth of the ω-precipitates is accompanied by a reduction of lattice strains due to an improved fit between β-matrix and ω-precipitates.

Furthermore, it was shown that the nucleation and growth conditions for ω-precipitates are significantly improved at a lower heating rate. Thus, pointing to the close relation of diffusion and the extent of the β- to ω-phase transition. It was
revealed that a slow heating rate of 1 K/min leads to a homogeneous and high density of medium-sized $\omega$-precipitates. It was also shown that existing compositional variations at the low heating rate are not of the same scale as the $\omega$-precipitates but larger compared to the higher heating rates. For a heating rate of 20 K/min, precipitation of incompletely transitioned $\omega_{\text{inc}}$-precipitates is still possible, but it appears that diffusion to a magnitude required to enable a complete transition into ideal $\omega$-phase is suppressed. Thus, leading to a homogeneous distribution and high density of $\omega_{\text{inc}}$-precipitates in the matrix. With a further increase in heating rate to 100 K/min, the formation of $\omega_{\text{inc}}$-precipitates is also reduced as evidenced by the low density of $\omega_{\text{inc}}$-precipitates. The reason for an incomplete $\omega$-phase transition is most likely insufficient diffusion at the higher heating rates.

6.2.3 Fast Cooling After Holding for One Minute at 823 K

A holding temperature of 823 K was selected to investigate the influence of heating parameters on $\alpha$-phase precipitation. The extent of $\alpha$-phase precipitation is related to microstructural development, growth directions and alloying element distributions for four different heat treatment plans. Three heat treatments followed continuous heating at rates of 1 K/min, 20 K/min and 100 K/min to 823 K respectively. In the fourth experiment a heating rate of 100 K/min was followed by an isothermal holding step for one hour at 623 K before continuing heating to 823 K at the same rate. Each sample was held for one minute at 823 K before it was fast cooled to room temperature. The latter experiment was designed to clarify the effects that $\omega$-aged material (held at 623 K) has on early $\alpha$-phase precipitation compared to the effects caused by the heating rate. The diffraction experiments discussed in Section 6.1 showed that $\alpha$-precipitation is advanced to different degrees at 823 K by different heating rates. The onset of the $\beta$- to $\alpha$-phase transformation occurred at 703 K for a heating rate of 1 K/min. Thus, the precipitation should be in an advanced state compared to the other samples where the $\beta$- to $\alpha$-phase transition occurred at 721 K for a heating rate of 20 K/min and at 685 K for the sample with an additional holding step at 623 K. leading to a significant ageing time difference of approximately two hours as compared to five or two minutes respectively. Finally, a
A heating rate of 100 K/min was found to start transforming after holding for about one minute at 823 K so that the α-precipitation should be at an early stage in this sample. The bright field images in Figure 79 confirm the different stages of β- to α-phase transformation at the respective heating rates. The image in the top left of Figure 79 shows homogeneously distributed, small, elongated α-precipitates in the β-matrix, taken for the sample heated at 1 K/min. In contrast the bright field image of the sample heated at 100 K/min on the bottom left of Figure 79 shows only the β-matrix. If any α-precipitates existed they would either be of such a small size that they cannot be observed at this magnification or they are in a state of incomplete transition, thus not leading to significant diffraction contrast. Interestingly enough the bright field images on the right of Figure 79 for a heating rate of 20 K/min (top) and 100 K/min, including the holding step 623 K (bottom), show very similar microstructures. In both cases very small α-platelets have grown in mainly two directions into the β-matrix. The growth directions will be discussed further in regard to the dark field images following below. The similar appearance of the microstructures indicates that the α-nucleation mechanism would have been very similar in both cases.
Figure 79: Bright field images after holding 1 min at 823 K and fast cooling to room temperature: Top Left: β-matrix with small α-precipitates (1 K/min); Top Right: β-matrix with tiny α-platelets (20 K/min); Bottom Left: β-matrix (100 K/min); Bottom Right: β-matrix with tiny α-platelets (100 K/min + Iso. Hold.)

The SAD patterns for heating rates of 1 K/min, 20 K/min and 100 K/min, but including the isothermal holding step at 623 K have similar appearances so that only the pattern for a heating rate of 20 K/min is shown in Figure 80. The pattern for a heating rate of 100 K/min is very similar to its pattern observed after cooling from 653 K (Figure 71) so that it is also not included in Figure 80. The SAD pattern in Figure 80 has intensity maxima on β- and α-positions for both α-variants. The cross-like distribution of intensity maxima in between β-reflects, is an indicator for α-precipitation where the central spot refers to one α-variant and the bright spot next to it belongs to the other α-variant. It has been shown by Guo et al. (2010) and Wu et al. (2006) that these reflections are typical for α-phase. A comparison to the key diagram on the right reveals that the outer edges of the cross do not overlap with ω-positions and from the previously presented diffraction results ω-phase would not be expected to be present in this stage of the heat treatment. A likely explanation for the extra α-reflects is the growth of α-platelets in other variants.
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Figure 80: SAD pattern of $<110>_{\beta}$-zone after heating at a rate of 20 K/min to 823 K, holding 1 min and fast cooling to room temperature.

That these extra reflections are caused by the $\alpha$-phase can be proven through dark field imaging. The objective aperture has been placed on the positions marked as g1 to g3 in Figure 80 (heating rate of 1 K/min) leading to the images given in Figure 81. The objective aperture covers one to three reflections so that similar regions are shown in the dark field images in Figure 81. Thus, the image in the centre (g1) shows mostly the $\alpha_2$-variant, the image on the left (g2) shows both $\alpha$-variants and the image on the right (g3) showing the $\alpha_1$-variant and a small region of the microstructure, which was not visible in the other two dark field images. This has been highlighted with arrows and it is evident that all three reflections are showing $\alpha$-precipitates.

The $\alpha$-precipitates are elongated particles of approximately 0.03-0.07 µm thickness, with the $\alpha_1$-variant growing close to $<\bar{1}10>_{\alpha_2}||<\bar{1}1\bar{2}>_{\beta}||<1\bar{1}0>_{\omega_2}$ and the $\alpha_2$-variant close to $<\bar{1}10>_{\alpha_1}||<\bar{1}1\bar{2}>_{\beta}||<1\bar{1}0>_{\omega_1}$. This agrees with results from Bhattacharyya et al. (2003) who have shown that favoured $\alpha$-nucleation will occur with $[001]_{\alpha}||[110]_{\beta}$ and $<\bar{1}10>_{\alpha}||<\bar{1}1\bar{2}>_{\beta}$ due to a reduction in energy of nucleus formation.
Figure 81: Dark field images for a heating rate of 1 K/min taken from the positions marked as g1, g2 and g3 in Figure 80: Left: g2 showing both α-variants; Centre: g1 showing α₂-position; Right: g3 showing α₁-position

The dark field images in Figure 82 were taken for a heating rate of 20 K/min and 100 K/min, which included the isothermal holding step at ω-ageing temperature from the position marked with a green spotted circle in Figure 80. The objective aperture covers reflections from both α-variants so that both appear in the dark field images. The thickness of the platelets is about 100-250 Å for a continuous heating rate of 20 K/min and 100-200 Å for the sample isothermally held at 623 K. The growth direction for these very fine α-precipitates is close to <112>β, but can deviate by a few degrees, which could be caused by lattice strains due to the early stage of α-precipitation. The deviation from <112>β for α-precipitates in the ω-aged sample appear slightly larger, which indicates that ω-precipitates may contribute to the observed deviation. Thus, the initial growth direction of α- and α′'-precipitates could be less dependent on the β-matrix if they were nucleating near or on ω-particles and then grew, while consuming these precipitates.
Figure 82: Dark field images taken from the position covering both α-variants marked in green in Figure 80

Figure 83 shows compositional maps of α-precipitates embedded in the β-matrix for a heating rate of 1 K/min. Two precipitates were analysed quantitatively by linescanning as shown in Figure 84 and Figure 85 respectively. It appears that diffusion of the β-stabilisers Fe and V into the β-matrix and the α-stabiliser Al into the precipitates is in an advanced state for a heating rate of 1 K/min. Some α-precipitates appear to have formed in β-stabiliser depleted zones advancing their growth while others are still forming and equilibrium has not been attained yet. This is particularly true for Fe since the concentration of Fe is almost zero in one precipitate, but the other precipitate contains up to 5 mass-% Fe inside and about 8 mass-% Fe in the transition area of matrix and precipitate. V is generally lagging behind the Fe-depletion, indicating that the rate of diffusion of V in β-Ti is lower than that of Fe (shown Figure 15 in Section 3.1.2). The same holds true for the enrichment of the α-precipitate with Al as its concentration increased up to 5 mass-% in one precipitate its concentration in the other precipitate is close to zero. These observations imply that different growth mechanisms operate in the precipitates, one precipitate could have nucleated in or near a β-stabiliser depleted zone, created during ω-formation and then grown into the depleted zone while the other could have nucleated somewhere else such as on another α-precipitate and did not grow into the β-stabiliser depleted zone. In order to get an estimate of the average phase
compositions further line scans were conducted as highlighted in the lower STEM image. The area highlighted in green gave an average composition of Ti-1.07Al-12.51V-8.88Fe (in mass-%) for the β-phase and the red area consisted of Ti-2.84Al-1.53V-0.52Fe (in mass-%) for the α-phase. These compositions confirm the advanced state of elemental distribution.

![Figure 83: EDS composition maps of the alloying elements overlayed with the STEM image of the area of interest shown in grey (1 K/min)](image)

![Figure 84: Results of the linescan for precipitate 1 in the STEM image in Figure 83 (1 K/min)](image)
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Figure 85: Results of the linescan for precipitate 2 in the STEM image in Figure 83 (1 K/min)

By comparison the higher heating rates did not allow for diffusion to occur at detectable levels and these results are therefore not included. The microstructures resulting from continuous heating at 20 K/min and 100 K/min (including holding step at 623 K) showed very similar appearances. Nevertheless, distinct differences show in the extent of diffusion in the two samples. The composition maps for a heating rate of 20 K/min is shown in Figure 86, followed by the results for the linescan in Figure 87 and the respective results for sample held at 623 K before continuing heating at 100 K/min are given in Figure 88 and Figure 89. The rate of β-stabiliser depletion in α-precipitates is lower in the sample heated at 20 K/min. Al-diffusion has not occurred to any measurable extent. In contrast the sample held at 623 K contains α-precipitates that are completely depleted in Fe, significantly reduced in their V-levels and possess an Al-concentration that is higher than the average of the β-matrix. These observations are in line with observations by Zheng et al. (2016b) who showed that α-precipitates nucleated on previously existing ω-precipitates are depleted in β-stabilisers. The sample heated continuously at 20 K/min contained ω_{inc}-precipitates, which were shown to possess a similar solute content as the β-matrix, thus preventing the full transformation into ideal ω-phase (see Figure 77 in Section 6.2.2). In contrast the sample held isothermally at 623 K before continuing heating would have formed completely transitioned ω-precipitates, which show a higher degree of diffusion. If the α-phase nucleates on or near these ω-precipitates and grows to
consume them this would explain the similar α-phase morphologies but differences in the extant of diffusion. These findings indicate that the morphology of early α-precipitates is mostly dependent on the nucleation spot density at the given ageing temperature. These outcomes are in line with studies by Duerig, Terlinde and Williams (1980) and Ohmori et al. (2001) on a Ti-10V-2Fe-3Al alloy who found that if heat treatment parameters promote a fine and homogeneous distribution of ω-precipitates of various orientations, the ω-phase precipitation will promote an α-phase precipitation, which will also consist of fine, uniformly distributed α-precipitates of various orientations. Thus, incompletely transitioned and fully transformed ω-precipitates can both promote α-phase nucleation in the Ti-1Al-8V-5Fe alloy if they are homogeneously distributed and exist in a sufficient density. Both types of ω-precipitates promote a similar α-morphology if heating rate and ageing conditions are comparable. The observation that α-phase is formed in similar ways regardless of the extent of β- to ω-phase transition indicates that the ω-transformation is reversed into β-phase first before α-precipitation occurs in this alloy. In this case the level of completion would not play a major role in the α-nucleation. This detail of the transformation sequence will be discussed further in line with the quantitative analysis of the diffraction data in Section 6.3.3 and 6.3.4.

The requirement for a high nucleation spot density explains the strong delay in α-nucleation for the sample heated at 100 K/min (without isothermal holding at 623 K). As detailed in the previous Section 6.2.2 the density of ωinc-precipitates was reduced in this sample, thus leading to a reduced number of α-nucleation spots. As a result α-precipitation is hindered to a degree that holding for one minute at 823 K does not lead to the nucleation of α-phase in detectable amounts.
Figure 86: EDS composition maps of the alloying elements overlayed with the STEM image of the area of interest shown in grey (20 K/min)

Figure 87: Results of the linescan marked in the STEM image in Figure 83 (20 K/min)
In summary, clear indicators exist that independent of the extent of the $\beta$- to $\omega$-phase transition, $\omega$-precipitates represent an important nucleation spot for $\alpha$-precipitates. Depending on the heating conditions these regions will be depleted of $\beta$-stabilisers, leading to $\alpha$-precipitates closer to their equilibrium condition. The morphology of the $\alpha$-precipitates appears more dependent on the ageing temperature than other heating parameters. For a heating rate of 1 K/min $\alpha$-nucleation sets in around 703 K,
which leads to rod-shaped precipitates, aligned closely to \(<112>\beta\), while heating at 20 K/min and 100 K/min (with isothermal holding) caused nucleation and growth of very fine platelet-like \(\alpha\)-morphologies. These platelets are found to nucleate parallel to each other in groups, aligned with \(<112>\beta\) directions.

### 6.2.4 Fast Cooling After Holding for One Hour at 823 K

A holding time of one hour at 823 K was chosen in order to compare the effect of prolonged holding on \(\alpha\)-phase precipitation, which nucleated under different conditions. Except for the holding time, the heat treatment plans were the same as in the previous section. Specimens were heated continuously at rates of 1 K/min, 20 K/min and 100 K/min to 823 K. A fourth specimen was heated at a rate of 100 K/min, then held isothermal for one hour at 623 K before continuing heating to 823 K at the same rate. Each specimen was held for one hour at 823 K before fast cooling to room temperature. The \(\alpha\)-phase precipitation in these specimens is compared with regard to \(\alpha\)-morphology, growth directions and alloying element distributions.

Holding for an hour at 823 K is sufficient to lead to an advanced state of \(\alpha\)-precipitation following a heating rate of 100 K/min. The STEM bright field image in Figure 90 shows the inhomogeneity of the microstructure resulting from this treatment. Embedded into the \(\beta\)-matrix are course, elongated \(\alpha\)-precipitates. One example is highlighted in yellow and has a thickness of about 0.45 \(\mu\)m. Smaller precipitates were also observed such as the one highlighted in green, which was about 0.053 \(\mu\)m thick. The distribution of \(\alpha\)-precipitates appears non-random. Some regions have a higher density of \(\alpha\)-precipitates growing in a star-shape fashion, but in close proximity to each other. These observations indicate that \(\alpha\)-nucleation at other \(\alpha\)-precipitates plays a strong role for a heating rate of 100 K/min. A few of these centres were marked in the figure. The significantly different microstructure following \(\alpha\)-precipitation, compared to the other heating rates, (detailed in the previous Section 6.2.3) might be attributed to the lack of \(\omega\)-enhanced \(\alpha\)-nucleation.

The low density of \(\omega\)-precipitates formed during heating at this high rate provides insufficient nucleation sites for the large amount of \(\alpha\)-phase that needs to form after
reaching 823 K in order to reach equilibrium. Hence, initially only a few α-precipitates are nucleated, which grow very quickly and thus reach much larger sizes than subsequently formed α-precipitates that can nucleate on those primary α-precipitates under a reduced driving force. These results are in line with findings by Dehghan-Manshadi and Dippenaar (2011) as well as Duerig, Terlinde and Williams (1980) who argued that an increase in ageing temperature leads to a type of sympathetic α-nucleation where α-phase precipitates on itself leading to a more inhomogeneous microstructure compared to α-nucleation on pre-existing ω-precipitates.

Figure 90: STEM bright field image after heating to 823 K with 100 K/min, holding for an hour and fast cooling to room temperature

The bright field images in Figure 91 show the microstructures for all four heat treatments in comparison. Exemplary α-precipitates have been highlighted in yellow for every image. The microstructure resulting for heating rates of 20 K/min and 100 K/min (including the isothermal holding at 623 K) are still of a very similar appearance. The precipitates have coarsened and appear stubbier now with a thickness of approximately 0.02 to 0.1 µm for a heating rate of 20 K/min and 0.02 to 0.07 µm in the other specimen. Some precipitates have changed to a more spherical shape. This effect is even more pronounced at 1 K/min with α-precipitates of approximately 0.08 to 0.15 µm in diameter. In contrast, the bright field image taken for the continuously heated sample at a rate of 100 K/min in the bottom left corner shows a significantly less dense population of much larger α-precipitates. The
smallest precipitates here are of a similar size as compared to the larger precipitates found in the other three microstructures. The growth direction for α-precipitates is found to be close to the <112>β-directions confirming observations made of α-precipitates nucleated under the other three heat treatments (Figure 81 and Figure 82 in Section 6.2.3).

Figure 91: Bright field images of β-matrix with embedded α-precipitates after holding an hour at 823 K and fast cooling for the different heat treatment parameters

The SAD pattern taken with a large aperture for a heating rate of 1 K/min show only β-phase reflections when aligned with the <110>β-zone axis so that the recorded pattern was not included. It does not mean that the α-phase does not exist or that it
would not follow the Burgers orientation to the β-matrix anymore. It indicates that the growth of the α-precipitates caused a local reduction of variants so that the particular two variants, which were aligned with the detected <110>β-zone axis do not continue to exist in the area where the SAD pattern was taken. This observation indicates that with continued growth of α-precipitates a local depletion of variants may occur. However, it does not allow to define the extent. The SAD patterns for the other three heating plans are very similar so that only the one recorded at a heating rate of 100 K/min is shown in Figure 92. The pattern shows β-reflections, reflections from both α-variants and faint additional spots most likely from other α-variants. In comparison to the SAD pattern recorded after holding for one minute at 823 K (Figure 80) the additional spots have slightly lost in intensity. This is an indication that the size of α-precipitates increased after holding for one hour at 823 K.

![SAD pattern of <110>β-zone after fast cooling after holding for an hour at 823 K with β and α-reflections for the different heat treatment plans: 20 K/min, 100 K/min, 100 K/min + Isothermal Holding](image)

Figure 92: SAD pattern of <110>β-zone after fast cooling after holding for an hour at 823 K with β and α-reflections for the different heat treatment plans: 20 K/min, 100 K/min, 100 K/min + Isothermal Holding

Dark field images were taken at the circled positions marked in Figure 92 from both α-variants for a heating rate of 20 K/min and the sample heated at 100 K/min with an additional holding step at 623 K. They are shown in Figure 93. The growth of the α-precipitates continues to follow <112>β. The stubby shape of the precipitates indicate that the smaller platelets shown in Figure 82 have combined to form these bigger precipitates while decreasing their thickness to length ratio. The precipitate
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morphology resembles the one found for α-precipitates heated by 1 K/min after reaching 823 K shown in Figure 81. This growth mechanism explains the more globular morphology found after prolonged holding for a heating rate of 1 K/min. It would be expected that the precipitates for a heating rate of 20 K/min and in the specimen held at 623 K behave similar for further extended holding times.

Figure 93: Dark field images of both α-variants taken from the positions marked in Figure 92: Left: Green circle, 20 K/min, Right: Blue circle, 100 K/min + Isothermal Holding

It can be observed that the α-morphology changes towards more globular shapes after prolonged holding. After precipitates in close proximity have combined to form bigger precipitates and the phase fractions are reaching near equilibrium conditions in respect to the holding temperature the driving force behind precipitate growth would be reduced significantly. Hence, the growth of precipitates at this point in time is mainly governed by diffusion. As diffusion should occur randomly in every direction it explains why over time the shape changes towards more spherical α-precipitates. These assumptions are confirmed when looking at the composition maps and the linescan results for a heating rate of 1 K/min shown in Figure 94 and Figure 95 respectively. The centres of α-precipitates are depleted of Fe and near depletion in the case of V with increasing β-stabiliser content towards the transition zone between matrix and precipitate and very high levels just outside the precipitates.
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Figure 94: EDS composition maps of the alloying elements overlayed with the STEM image of the area of interest shown in grey (1 K/min)

Figure 95: Results of the linescan marked in the STEM image in Figure 94 (1 K/min)

An enrichment of V and Fe just outside the α-precipitates can also be observed for a heating rate of 20 K/min shown in Figure 96 and Figure 97. The linescan clearly shows that while the centre of the precipitate is close to β-stabiliser depletion the area in between precipitate one and two (around 2000 Å distance) contains almost twice the β-stabiliser content. Thus, causing the growth of precipitates to slow down significantly while making it more dependent on diffusion at the same time.
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Figure 96: EDS composition maps of the alloying elements overlayed with the STEM image of the area of interest shown in grey (20 K/min)

![Figure 96](image)

Figure 97: Results of the linescan marked in the STEM image in Figure 96 (20 K/min)

![Figure 97](image)

The composition maps and the linescan results for a heating rate of 100 K/min in Figure 98 and Figure 99 show that this specimen differs from the previously described specimens. Here, the driving force of transforming into \(\alpha\)-phase was very high due to the elevated temperatures during the \(\alpha\)-phase nucleation so that the phase transition would have occurred first, followed by diffusion. Therefore, the level of \(\beta\)-stabiliser depletion inside the \(\alpha\)-precipitates is about 2-3 mass-% for Fe and about 5 mass-% for...
V and the β-matrix is also not as strongly enriched in Fe and V with levels of about 7 and 10 mass-% respectively.

In conclusion, it was shown that the lack of ω-enhanced α-nucleation leads to an inhomogeneous microstructure in the sample heated by 100 K/min after holding for an hour at 823 K. Thus, a wide distribution of sizes is found and it appears that the limited nucleation spots caused primary precipitation of very big α-precipitates.
followed by self-induced secondary, smaller $\alpha$ precipitates growing from there. Nevertheless, the growth direction for $\alpha$-precipitates was found to be close to $<112>_{\beta}$ again. Furthermore, it was found that prolonged growth of $\alpha$-precipitates in the case of a heating rate of 1 K/min leads to a change of $\alpha$-morphology towards a more spherical shape. This change in precipitate shape is explained by the dependence of growth on diffusion, leading to a more random growth direction.

6.2.5 Conclusions from Ex-Situ High-Resolution Scanning Transmission Electron Microscopy Studies

The results of the ex-situ TEM study show a correlation between heating rate, diffusion and the extent of $\beta$- to $\omega$-phase transition in the Ti-1Al-8V-5Fe alloy. It was shown that a heating rate of 1 K/min produces homogenously distributed, well-developed $\omega$-precipitates up to $\sim$50 Å in diameter at temperatures below 593 K that transform following an orientation relationship to the surrounding $\beta$-matrix. Due to the necessity of the matrix to incorporate differing variants of $\omega$-phase in close proximity a mismatch below 1° was found between $\{001\}_\omega$ and $\{111\}_\beta$ indicating lattice strains resulting from the $\omega$-precipitation. With increasing $\omega$-ageing time due to continued heating to 653 K these lattice strains were found to disappear as the growth of $\omega$-precipitates to more globular particles with diameters of 70 to 110 Å is accompanied by a reduction of variants causing an improved fit between matrix and precipitates. Furthermore, it was shown that the extent of diffusion due to the different heating rates is affecting the state of the $\beta$- to $\omega$-phase transformation. Compositional variations exist randomly distributed throughout the matrix for a heating rate of 1 K/min, which are not of the same scale as the $\omega$-precipitates but still of a larger magnitude as compared to the higher heating rates. These conditions allow for a high density of homogeneously distributed, medium-sized, fully transformed $\omega$-precipitates. It was also shown that compositional variations for the higher heating rates are so small that they are nearing the technical error of the technique so that they either do not exist or cannot be detected. Thus, a complete $\beta$-to $\omega$-phase transformation is inhibited for heating rates of 20 K/min or higher. However, it was found that the dependency of nucleation of $\omega$-phase on diffusion is of a lower magnitude, thus, leading to a homogeneous and high density of
incompletely transitioned $\omega_{\text{inc}}$-precipitates in the matrix of very small size for the sample heated by 20 K/min. With a further increase in heating rate to 100 K/min the nucleation of $\omega$-phase is also reduced as evident through the low density of $\omega_{\text{inc}}$-precipitates.

In regard to the $\alpha$-phase transformation in the Ti-1Al-8V-5Fe alloy it was found that the morphology of precipitates is governed mainly by the holding temperature and time as well as the history of the sample that is affecting $\alpha$-nucleation kinetics. It was shown that diffusion does not play a strong role in early $\alpha$-nucleation as $\alpha$-precipitates showed a very similar shape and distribution for a heating rate of 20 K/min as well as the sample that had been heated by 100 K/min but held at 623 K for an hour before continued heating to the final $\alpha$-ageing temperature at 823 K. The level of $\beta$-stabilisers within $\alpha$-precipitates in the continuously heated sample were higher than in the material held at 623 K showing that the provided nucleation spot density is of much higher importance than the local composition in enabling early $\alpha$-nucleation.

Fully developed $\omega$-precipitates as well as incompletely transitioned precipitates are suited to enhance $\alpha$-nucleation kinetics leading to an initial microstructure of homogeneously distributed, very fine $\alpha$-platelets with a thickness of approximately 150 Å after holding for one minute at 823 K. After prolonged holding for an hour these platelets have grown into much stubbier precipitates with an approximate thickness of 0.05 µm. In contrast, the lack of $\omega$-enhanced nucleation leads to a strong delay in $\alpha$-nucleation in the sample heated continuously by 100 K/min. So that after holding for an hour at 823 K the microstructure is very inhomogeneous. Very large $\alpha$-precipitates have formed first, which improved the nucleation conditions so that the following secondary $\alpha$-precipitates are of much smaller sizes. Thus, leading to a size distribution of elongated particles between 0.053 µm and 0.45 µm.

For all heating conditions it was found that the elongated particles are aligned with $<112>_{\beta}$. For the specimen heated at 1 K/min to 823 K the $\alpha$-precipitates are of a stubby morphology with a thickness of 0.03-0.07 µm. It was found that prolonged growth of these $\alpha$-precipitates leads to a change of $\alpha$-morphology towards a more spherical shape with diameters of 0.08 to 0.15 µm.
6.3 Analysis on the effect of heating parameters on phase transformations in Ti-1Al-8V-5Fe

This section aims to analyse quantitatively the phase transformations occurring during different heat treatments. In Section 6.3.1, the extent of the β- to ω-phase transition is characterised with regard to the {111}_β plane collapse.

The effect of an intermediate ω-phase transition on the formation of α-phase was analysed through single peak and Rietveld fitting of the diffraction data and the determined phase fraction developments are presented in Section 6.3.2 and 6.3.3 respectively. The Rietveld method using MAUD software enabled the determination of the lattice parameter evolution, which is discussed in Section 6.3.4 under consideration of the influence of lattice strains as well as compositional changes as effected by the phase transformations.

6.3.1 Extent of the ω-transformation as influenced through the heat treatment conditions

The diffraction studies discussed in Sections 6.1 and 6.2 showed diffuse intensity distributions at various temperatures in diffraction patterns, which were attributed to the tendency of the bcc lattice for atomic displacements in <111>_β directions. These deviations from atomic positions can be understood as a precursor of the ω-phase transition. At high temperatures lattice faults in <111>_β directions remain uncorrelated, thereby inhibiting an ω-phase transition. The crystal structure is fully β-phase because local atomic shifts exist but remain unstable. During quenching these structural fluctuations are frozen-in and begin to correlate to form ω_{inc}-precipitates during subsequent heat treatments. For heating rates of 5 K/min or an intermediate holding temperature at 623 K the ω_{inc}-phase was shown to transition into a fully developed ω-phase. This Section aims to characterise the extent of ω-phase transition for the different heat treatment parameters by determining the atomic shift in relevant lattice directions.

As explained in detail in Section 2.5 the β- to ω-phase transformation is achieved by a displacement of atoms in the <111>_β direction. For a fully developed ω-phase every second and third {222}_β plane need to merge so that the stacking sequence of {222}_β
planes alters from ...A-B-C-A-B-C-... to ...A-B'-A-B'-... Thus, atoms in A planes remain in their positions whereas atoms in B and C planes need to shift by 0.5 $d_{\{222\},\beta}$ to form $B'$ planes. The atomic motifs for varying degrees of $\{111\}_\beta$ plane collapse are shown in Figure 100 as seen from the $<110>_\beta$ direction. The figure shows that the required atomic movement to achieve $\{111\}_\beta$ plane collapse not only changes atomic positions in the $<111>_\beta$ direction but also effects atomic positions in the $<001>_\beta$ direction. Thus, within the $\beta$-phase atomic distances should be constant along the $<001>_\beta$ direction whereas in the $\omega$-phase a set of three planes would still possess the same width along the $<001>_\beta$ direction but the atomic distances among these planes would follow a short, long, long sequence. Using High-Resolution TEM (HRTEM) methods the extent of these atomic shifts was determined to achieve an indication for the degree of plane collapse and thus the extent of the $\beta$- to $\omega$-phase transformation. The direction along $<001>_\beta$ used to determine the extent to which the $\omega$-transformation is completed, is highlighted in yellow in the atomic motifs in Figure 100.

Figure 100: Atomic motifs of $\beta$-, incomplete $\omega$- and ideal $\omega$-phase, highlighting $<001>_\beta$ and $<111>_\beta$ used to determine the degree of the $\{111\}_\beta$ plane collapse

The atomic shift along $<001>_\beta$ was measured at room temperature for a fully developed $\omega$-precipitate in the sample discussed in Section 6.2.2, which had been heated at 1 K/min to 653 K. The Fourier filtering image of the high-resolution image of the lattice is shown in Figure 101. It shows the atomic motifs and directions for
both β- and ω-phases, where atomic positions appear white due to their high intensity levels. The intensity variations and thus atomic distances in <001>β were measured along the blue row and are plotted in Figure 102. The β-phase on the left shows very regular atomic distances and from a distance of about 16 Å, the lattice changes towards ω-phase, which results in a more irregular arrangement of these atomic positions. Simultaneously with the change in interatomic distances, a significant change in the intensity distribution of atoms and the spaces in between them is observed. The atomic shift in <111>β causes the atomic centres to deviate from <001>β (shown in Figure 100). The measured distances for one set of atomic distances in the β- and ω-phases are plotted in Figure 103. Each set of three consecutive planes has the same width of ~4.8 Å in β- and ω-phase. The atomic distances between {002}β-planes are very regular in the β-phase and around 1.6 Å. An interplanar spacing of {002}β-planes (d_{002β}) of 1.6 Å agrees well with the β-lattice parameter a_β = 3.23 Å determined from diffraction results. As expected the atomic distances in the ω-lattice alter between 1.3 Å for the shorter distance and 1.7-1.8 Å for the two longer distances. These outcomes agree well with findings of Devaraj et al. (2012) who studied the structure of the ω-phase in Ti-Mo alloys.

Figure 101: Fourier filtering of the crystal lattice of a fast cooled sample, which was heated at 1 K/min to 653 K
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Figure 102: Interatomic distances along the $\langle 001 \rangle_\beta$ direction with $\beta$-phase on the left and $\omega$-phase on the right

Figure 103: Interatomic distances along the $\langle 001 \rangle_\beta$ direction with $\beta$-phase on the left and $\omega$-phase on the right

Even though measurements along $\langle 001 \rangle_\beta$ provide a clear indication of the degree of the $\beta$- to $\omega$-phase transformation, they only offer qualitative information. As the $\{111\}_\beta$ plane collapse occurs in the $\langle 111 \rangle_\beta$ direction the extent of collapse can only be quantified in that direction. Figure 100 shows that atoms in $\{222\}_\beta$-planes on B and C positions need to shift by $0.5 \ d_{222\beta}$ to form the $\{002\}_\omega$-plane of the ideal $\omega$-phase, which is indicated as B’ whereas atoms on A-planes maintain their positions. One $\langle 111 \rangle_\beta$ direction was highlighted in Figure 100. The Fourier filtered image of the
lattice is shown in Figure 104. The image is of the same sample, which had been used for the determination of atomic shifts along <001>β. It shows the motifs and directions for both the β- and ω-phases. The interatomic distances in <111>β are measured along three atomic rows highlighted in blue. The interatomic distances are plotted in reverse order in Figure 105 to show the development from β-phase on the left to ω-phase on the right. To enable measurement of the atomic position shift the first atomic position in the β-phase in each row was brought to overlap. The β-phase on the left shows very regular interatomic distances and from about -33.6 Å the lattice starts changing to the ω-phase. The peak distances for each phase are ~2.7 Å and as this distance is equal to 3d_{222β}, it follows that d_{222β} ≈ 0.9 Å, which agrees with the calculated d-spacings from: d_{222β} = 1/√12a_β ≈ 0.93 Å. With d_{001ω} = 3d_{222β}, c_ω is calculated to be 2.7 Å, which agrees well with results from diffraction experiments of 2.78 Å for a fully transformed ω-phase. The atomic positions in row 1 are expected to maintain the same whereas positions in row 2 and 3 would be shifted by 0.5d_{222β} ≈ 0.45 Å to the right and left respectively in order to achieve a full plane collapse. Exemplary peak positions for the β- and ω-phases are shown in Figure 106, including the measured peak shift in the ω-lattice for one set of interatomic distances, indicating the full collapse of {222}_β. These results clearly show that peak positions in the β-phase remain overlapped for all three rows while a full shift between 0.4 and 0.5 for the respective rows was observed after only a few interatomic distances indicating a fully transformed ω-phase. These outcomes also agree with previous results of Devaraj et al. (2012) for fully transformed ω-precipitates in Ti-Mo alloys.
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Figure 104: Fourier filtered image of the crystal lattice of a fast cooled sample, which was heated at 1 K/min to 653 K.

Figure 105: Interatomic distances along three consecutive rows in the $<111>_{\beta}$ direction with $\beta$-phase on the left and $\omega$-phase on the right.
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Figure 106: Interatomic distances along three consecutive rows in the $\langle 111 \rangle_\beta$ direction with $\beta$-phase on the left and $\omega$-phase on the right

These results show that a heating rate of 1 K/min is sufficiently slow to allow for an intermediate $\beta$- to ideal $\omega$-phase transformation, which will appear as discrete, but broad peaks in synchrotron and neutron diffraction patterns and diffract as discrete intensity maxima on $\omega$-positions in SAD patterns.

Next, the extent of $\beta$- to $\omega$-phase transformation shall be determined for an incompletely transitioned $\omega_{inc}$-precipitate that was found in a sample detailed in Section 6.2.2. The sample was heated at a rate of 100 K/min to 653 K before fast cooling. First, the atomic shift in the $\langle001\rangle_\beta$ direction was analysed. The Fourier filtered image in Figure 107 shows the crystal lattice with atomic motifs of the $\beta$-phase and $\omega_{inc}$-phases. The row highlighted in blue was used to measure the atomic positions along $\langle001\rangle_\beta$ and the results are given in Figure 108 for the full row and in Figure 109 for a short interatomic distance in the $\beta$-phase on the left and the $\omega_{inc}$-phase, in the centre of the precipitate, on the right. The interatomic distances in the $\beta$-phase are very regular and about 1.6 Å. From about 16 Å on, intensity variations of atomic positions indicate an atomic shift towards $\omega$-positions. However, the shift is small compared to the fully transformed $\omega$-phase presented in Figure 103 and only slightly larger than the shift in the $\beta$-phase. Thus, highlighting the incomplete transition of this precipitate.
Figure 107: Fourier filtering of the crystal lattice of a fast cooled sample, which was heated at 100 K/min to 653 K

Figure 108: Interatomic distances along the $<001>_{\beta}$ direction with $\beta$-phase on the left and $\omega_{inc}$ on the right
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Figure 109: Interatomic distances along the <001>β direction with β-phase on the left and ωinc on the right

In order to quantify the extent of the transition another measurement was done on this precipitate along <111>β. The three rows shown in the Fourier filtering of the crystal lattice in Figure 110 have been used to determine atomic positions in <111>β. The first atomic position of the β-phase has been brought to overlap and results for the full rows are given in Figure 111. Atomic positions of the β-matrix (left) and the centre of the ωinc-precipitate (right) are compared in Figure 112. In this case atoms in row three maintained static positions while atoms in the first and second row have started shifting to lower or higher positions respectively. Here, the distance between two peaks was determined as 2.77 Å, which is very close to the previously found value of 2.67 Å in the sample heated at 1 K/min. However, the peak shifts of 0.1 Å and 0.23 Å are only totalling to a shift of 0.33 Å between the first two rows. As explained before the ideal ω-phase is achieved by a total shift of 0.9 Å so that the degree of the β- to ω-phase transition accomplished in this sample is only about one third. The incomplete phase transition in this sample is caused by the faster heating rates. The ωinc-phase does not possess a definite structure and hence, cannot diffract into defined peaks but would lead to increased background by contributing to the diffuse scattering of the sample. This explains the diffuse intensity distributions found in SAD, neutron or synchrotron diffraction patterns heated at heating rates of 20 K/min or higher.
Figure 110: Fourier filtering of the crystal lattice of a fast cooled sample, which was heated at 100 K/min to 653 K

Figure 111: Interatomic distances along three consecutive rows in the <111>$_{\beta}$ direction with $\beta$-phase on the left and $\omega_{inc}$-phase on the right
Figure 112: Interatomic distances along three consecutive rows in the $<111>_{\beta}$ direction with $\beta$-phase on the left and $\omega_{\text{inc}}$-phase on the right

Finally, a sample after quenching from the $\beta$ transus shall be investigated. As detailed in Section 6.1.1 diffuse scattering could be observed in both the neutron and electron diffraction patterns. The diffuse intensity distributions are explained by uncorrelated atomic displacements in the $<111>_{\beta}$ direction to positions closer to their respective positions in the $\omega$-phase and represent precursors to the $\omega$-phase transition. However, in this stage before heating most atoms still maintain their $\beta$-lattice positions. As atomic displacements from regular $\beta$-positions lie in the $<111>_{\beta}$ direction, it would be expected to find only uncorrelated and somewhat chaotic deviations in other lattice directions. On the other hand atomic positions in the $<111>_{\beta}$ direction are expected to follow regular distances within each row with a potential (but uncorrelated) shift in respect to each other (from one row to the next). Hence, indicating local deviations from $\beta$-phase positions, which are understood as precursors of $\omega$-phase transition.

These assumptions are confirmed by the measurements. The measurement in the $<001>_{\beta}$ direction given in Figure 113 with results following in Figure 114 and Figure 115 show that the interatomic distances are comparatively irregular and fit neither distinct $\beta$-phase positions nor the $\omega$-phase positions. A set of three atomic columns has a width varying from 4.7 to 5 Å where most sets have a width of about 4.8 Å. This clearly shows a loss in constancy compared to the $\beta$-phase in other samples discussed with reference to Figure 102 and Figure 108. Most interatomic spacings are very close to the expected values for the $\beta$-phase of 1.6 Å and the short, long, long distance
pattern found in (partially) \( \omega \)-transitioned regions for the previous samples cannot be verified here often. The set of atomic positions given on the right of Figure 115 was followed by a distance of 1.6 Å (not shown) and thus returned to a \( \beta \)-positioning in the fourth column. These variations even within a few interatomic distances confirm assumptions about the somewhat more chaotic pre-transitional state of this structure.

![Figure 113](image1.png)

**Figure 113:** Fourier filtering of the crystal lattice of the as-quenched condition after the \( \beta \)-solution treatment

![Figure 114](image2.png)

**Figure 114:** Interatomic distances along the \( \langle 001 \rangle_\beta \) direction
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Interatomic distances were also determined for three adjacent rows in the \textit{<111>}_\beta direction (Figure 116) to enable quantification of the extent of the \( \beta \)- to \( \omega \)-phase transition. For the analysis first atomic positions were brought to overlap and the measurements are presented in Figure 117 and Figure 118. Interatomic distances within each row are very regular and approximating 2.77 Å. The two samples detailed with reference to Figure 105 and Figure 111, where the \( \beta \)- to \( \omega \)-phase transitioned was at least partially accomplished, showed a correlation between atomic positioning in the neighbouring rows. These observations are in contrast to findings from the current sample in Figure 117 and Figure 118. The right of Figure 118 shows a region, in which atomic columns in row 2 are deviating by up to 0.16 Å in regard to the other two rows, whilst maintaining regular interatomic distances of 2.77 Å within the row itself. However this displacement is uncorrelated to atomic positioning in the other two rows. Atomic columns in both rows maintain their positions, which would not be the case for a (partial) \( \beta \)- to \( \omega \)-phase transition. So that row two shows local displacive ordering of atoms approximating \( \omega \)-positions but uncorrelated with respect to neighbouring rows. These findings confirm uncorrelated atomic displacements in the \textit{<111>}_\beta direction and are therefore identified as a precursor of \( \omega \)-phase transition.
Figure 116: Fourier filtering of the crystal lattice of the as-quenched condition after the β-solution treatment

Figure 117: Interatomic distances along three consecutive rows in the $<111>_{\beta}$ direction
Figure 118: Interatomic distances along three consecutive rows in the \( <111> \)\_B direction with \( \beta \)-phase on the left and an example of a precursor for \( \omega \)-nucleation on the right.

The analysis of the extent of the \( \omega \)-phase transition of the as-quenched \( \beta \)-phase following the \( \beta \)-solution treatment identified precursors of \( \omega \)-phase transition. Here, on a scale of a few interatomic distances columns of atoms would deviate from their respective positions in the \( <111> \)\_B directions thus approaching positions of the \( \omega \)-phase. However, in this stage displacements are uncorrelated between neighbouring rows, leading to more chaotic atomic positioning in other lattice directions. During heating these displacements in the \( <111> \)\_B direction start to correlate. A heating rate of 1 K/min led to the formation of an ideal \( \omega \)-phase, while heating rates of 20 K/min and higher only enabled a partial transformation into \( \omega \)\_inc-phase. The combination of these findings with the observations presented in Section 6.1.1 and 6.2.2 lead to the conclusion that to achieve a full \( \beta \)-to \( \omega \)-phase transformation a degree of diffusion is required that cannot be provided under an applied heating rate of 20 K/min and higher. Thus, clearly indicating that the \( \beta \)-to \( \omega \)-transition is a phase transformation where atomic shuffling is followed by diffusion, followed by further atomic shuffling and so on.

### 6.3.2 Quantitative Analysis of the Phase Fraction Development by Single Peak Fitting

The effect of an intermediate \( \omega \)-phase transition on the \( \beta \)-to \( \alpha \)-phase transformation was analysed through single peak fitting of the neutron diffraction data presented in Section 6.1.2.2 and 6.1.3.2. The development of the integrated peak area over time
is used to track the phase evolution over time. The calculated phase fractions over time for the $\alpha$-phase ($X_a$), $\beta$-phase ($X_b$) and $\omega$-phase ($X_o$) are plotted in Figure 119 and Figure 120 for heating rates of 1 K/min and 20 K/min respectively. Two different $\alpha$-phase fractions (red and yellow) were plotted. The red $X_a$ followed from the observation that the only phases present at the end of the experiment were $\alpha$- and $\beta$-phases and was therefore calculated as $1 - X_b$. The yellow $X_a$ was derived from the integrated peak area of an $\alpha$-peak. It should be noted that single peak fitting methods do not allow differentiation between $\alpha''$- and $\alpha$-phase reliably due to the peak overlap so that the analysis was run under the assumption that $\alpha$-phase is directly formed from $\beta$-phase.

![Phase fraction vs. Time](image)

**Figure 119:** Phase evolution during heating at a rate of 1 K/min to 823 K
Figure 120: Phase evolution during heating at a rate of 20 K/min to 823 K

The plots show that amount of α phase precipitated during the holding time at 823 K is in both cases about 40% and the phase fraction further increases during slow cooling. Figure 119 shows an intermediate increase in the fraction of β-phase just before 400 min into the measurement, which is likely due to an overlap with an ω-peak at this position. An increase in heating rate from 1 K/min to 20 K/min led to a delay of the α-phase transformation of about 70 K from approximately 650 K to 720 K.

Single peak fitting is useful to produce quick results indicating major microstructural changes. However, wide ω-peaks were hard to fit with this method and the α”-phase fraction couldn’t be determined. Single peak fitting in the absence of additional information from Rietveld fitting does not produce results of the same level of reliability, hence the analysis was furthered with the Rietveld method.

6.3.3 Phase Fraction Analysis through Rietveld Refinement

As detailed in Section 4.2.2 the Rietveld method takes the crystallographic structure of the different phases into account and thus presents an advanced analysis technique. In addition, the Rietveld technique will account for every peak of a phase and thus give an average value of the phase fraction or the lattice parameter. The synchrotron experiment detailed in Section 6.1.2.1 in, which the sample was heated
at 5 K/min to 823 K was analysed through a consequent Rietveld refinement. Here, the parameters of interest such as phase fractions or lattice parameters are improved to a best fit for every data file of the experiment using the fit of the preceding file as starting values. The refined values can then be employed for experimental evaluation by plotting data of interest over experimental parameters such as time or temperature. The mean value of the least square fitting ($R_b$) is 7.4 % indicating an acceptable fit of the refinement to the data, which is comparable to a maximum of 8 % achieved by Barriobero-Vila et al. (2015a) in a study of the Ti-5Al-5Mo-5V-3Cr-1Zr alloy.

The phase fractions obtained through Rietveld refinement are plotted over temperature in Figure 121. This relatively slow heating rate enabled phase transitions of $\beta$- to $\omega$- and $\alpha''$-phases before a stable $\alpha$-phase is precipitated. The results show that $\omega$-phase starts precipitating at 550 K and reaches a maximum fraction of 34.7 mass-% at about 650 K. The $\beta$-phase fraction opposes the trend of the $\omega$-phase up to 696 K. At 696 K the $\omega$-phase fraction drops with a concomitant increase of $\alpha''$-phase fraction and later also $\alpha$-phase fraction. Between 696 K and 712 K the amount of $\beta$-phase increases from 70 % to 75.5 %, indicating that a small fraction of $\omega$-phase dissolves back into the $\beta$-matrix while $\alpha''$-precipitates grow to consume the $\omega$-precipitates. From about 725 K on, the $\beta$-phase fraction slowly decreases while the fraction of $\alpha$- and $\alpha''$-phase increase, leading to a $\beta$- to $\alpha$-phase ratio of 66.4 to 33.6 % upon reaching 823 K.
Figure 121: Phase evolution from high energy X-ray data during continuous heating at 5 K/min to 823 K

In conclusion, the phase transformation sequence for a low heating rate follows the sequence shown in Equation (32). The phase fraction analysis confirms TEM observations presented in Sections 6.2.3 and 6.2.4, which indicate that α”-phase is likely to nucleate in or near ω-precipitates and grows to consume the ω-phase although some of the ω-precipitates dissolves back into the matrix. This points toward the ω- to α”-phase transformation following the sequence given in Equation (33). This observation will be clarified further in Section 6.3.4 with regard to the lattice parameter development.

\[
\beta \rightarrow \beta + \omega \rightarrow \beta + \omega + \alpha'' \rightarrow \beta + \alpha'' \rightarrow \beta + \alpha'' + \alpha \rightarrow \beta + \alpha \quad (32)
\]

\[
\omega \rightarrow \beta \rightarrow \alpha'' \quad (33)
\]

The phase fraction development points to the α-phase formation from α”-phase. This observation is confirmed by the consideration of required lattice strains to accommodate those structures within the β-phase, which will be evaluated in detail in Section 6.3.4.1.

As shown in Section 6.1.3.1 an increase in heating rate to 100 K/min suppresses ideal ω-formation and delays initial α”-nucleation to 30 s holding at 823 K. The reason for an incomplete ω-phase transformation to \( \omega_{inc} \)-phase can most likely be found in the high solute content of this alloy. The high amount of Fe and V stabilises the β-phase, hence limiting conditions of ideal ω-phase formation. Therefore, low heating rates that allow for sufficient alloying element diffusion to locally destabilise the β-matrix and thus enhance transformation are required for a full β- to ω-phase transition. The low density of \( \omega_{inc} \)-phase precipitates formed during heating at 100 K/min influences the kinetics of α”-precipitation. As a result, the β- to α”-phase transition is delayed by approximately 130 K to the isothermal holding step at 823 K as compared to an α”-phase transition at a heating rate of 5 K/min, which was discussed previously with reference to Figure 121.

Lowering the heating rate to 20 K/min improves the conditions for the β- to ω-phase transition. The transition remains incomplete, but the density of \( \omega_{inc} \)-precipitates
embedded within the β-phase increases significantly. This neutron diffraction experiment was described in Section 6.1.3.2. As shown in Section 6.3.1 the ωinc-precipitates that form at a heating rate of 20 K/min resemble the non-ideal type of ω-phase where the {111}β plane collapse is incomplete. Atomic positions in β-directions are shifted in the ωinc-phase, but not to the same extent as in the ideal ω-structure. Thus, the crystal structure is in between the β-phase and the hexagonal ω-phase and is best described as trigonal (see Section 2.5). As explained above the incomplete collapse originates in the reduced extent of β-stabiliser diffusion thus preventing a full β- to ideal ω-phase transformation. Atomic shifts in β-phase directions (ωinc-phase) lead to the appearance of β-peak shoulders in diffraction patterns, as discussed with reference to Figure 46. The appearance of β-peak shoulders has been identified as an intermediate ω-phase transition in Ti-5Al-5Mo-5V-3Cr alloy by Jones et al. (2009). The Rietveld technique identified this non-ideal ω-phase, which allowed a complete phase fraction analysis including the ωinc-phase for a heating rate of 20 K/min as shown in Figure 122.

![Figure 122 Phase evolution from neutron data during continuous heating at 20 K/min to 823 K](image)

At a heating rate of 20 K/min ωinc-phase forms from about 550 K to 650 K on, when the ω-fraction decreases strongly and disappears at 675 K compared to 730 K when heated at a rate of 5 K/min. The earlier disappearance of the ωinc-phase is most likely due to its limited stability caused by the incomplete stage of the structural transition as compared to the ideal ω-phase found at a lower heating rate. The α″-phase forms
below 675 K and reaches an \((\alpha^{\prime\prime} + \alpha)\)-phase fraction near the maximum amount at about 720 K. The appearance of \(\alpha^{\prime\prime}\)-phase coincides with the disappearance of \(\omega\)-phase and a slight increase in \(\beta\)-phase fraction. It seems that at least a part of the \(\omega\)-phase transforms back into \(\beta\)-phase before \(\alpha^{\prime\prime}\)-phase nucleates. This observation will be discussed further in Section 6.3.4. Furthermore, the observed \(\alpha\)-phase fraction is high with a maximum amount of 59 mass-% compared to 33.6 % found for synchrotron data at a heating rate of 5 K/min. As explained in Section 6.1.2.2 this is due to the enrichment of the \(\beta\)-phase with Fe, which effects the neutron scattering ability of the \(\beta\)-phase. This will be analysed in detail further below with reference to Table 9 and Table 10.

Finally, the phase evolution for the neutron diffraction experiment detailed in Section 6.1.4 has also been determined as shown in Figure 123. Here, the sample was heated at a heating rate of 20 K/min and held isothermally for 70 min at 623 K before continuing heating at the same rate to 823 K. Again the \(\omega_{\text{inc}}\)-phase appears around 515 K. However, the \(\omega_{\text{inc}}\) to ideal \(\omega\)-phase transition is completed during holding at 623 K. In the diffraction pattern this transition is evidenced by the appearance of distinct peaks on \(\omega\)-phase positions (Section 6.1.4). During holding at 623 K the \(\omega\)-phase fraction reaches a maximum of 47 mass-%. Following heating at a rate of 20 K/min, the \(\omega\)-fraction decreases slowly at first and then more rapidly due to the concomitant \(\alpha^{\prime\prime}\)-phase formation from 685 K onwards. The temperature range for the coexistence of the \(\omega\)- and \((\alpha^{\prime\prime} + \alpha)\)-phases increased to 25 K compared to 20 K in the experiment without the additional holding step. Even though the difference is rather small it confirms the importance of the degree of structural transition in the \(\omega\)-phase stability as caused by the holding at 623 K. The maximum amount of \((\alpha^{\prime\prime} + \alpha)\)-phase fraction of 58 mass-% is reached at 815 K. In contrast, in the experiment without an intermediate holding step the same fraction was reached at 765 K. This observation indicates that higher \(\omega\)-phase stability causes a slower \((\alpha^{\prime\prime} + \alpha)\)-phase growth. The most plausible cause for this delay of 50 K is the depletion of \(\omega\)-precipitates in \(\beta\)-stabilisers during holding, which slows down the reverse phase transformation into \(\beta\)-phase and thus hinders the \((\alpha^{\prime\prime} + \alpha)\)-phase transition.
The increased solubility for Fe in the β-phase leads to an enrichment during the β- to ω- and β- to α-phase transitions. This change in composition affects the neutron scattering ability of the material and thus the intensity levels of the respective phases. As explained in Section 4.1.1 the neutron scattering ability of a material depends on the sum of the scattering lengths of the elements it contains. Titanium has a negative scattering length while iron has a positive scattering length. Thus, a substitutional enrichment of iron in titanium would result in decreased Bragg scattering in the case of neutron diffraction. Therefore, the enrichment of the β-phase in Fe in line with the ω- and α’”- phase transitions is effecting the respective phase’s ability to scatter neutrons. So that the real phase fractions for (α’”+α)- and ω-phase are expected to be lower due to the influence of Fe on the neutron diffraction signal.

In order to approximate the influence of composition on the neutron scattering abilities of the respective phases the coherent scattering cross sections $\sigma_c$ were calculated following Equations (18) and (19) for the β-phase at the beginning of the experiment and at 823 K in coexistence with the α-phase. The composition of the respective phases at 823 K was determined in Section 6.2.3 with reference to Figure 83. The resulting $\sigma_c$ for each composition are listed in Table 9 together with the factor that the respective phase fraction needs to be divided by to correct it for the change in scattering ability. After applying these correction factors to the phase fractions determined through Rietveld fitting of the neutron data at 823 K and normalising...
them to sum up to 100% the values are very close to the results determined from the high energy X-ray experiment at a heating rate of 5 K/min (Table 10). Therefore, this correction is assumed to be correct as long as the phase compositions are approximated by the values listed in Table 9.

Table 9: Composition for the β-phase as a sole phase and together with the α-phase at 823 K, σc and the resulting correction factor that needs to be applied to the respective phase fraction

<table>
<thead>
<tr>
<th>Composition / mass-%</th>
<th>β-phase (sole phase)</th>
<th>β-phase (with α-phase at 823 K)</th>
<th>α-phase (at 823 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-1.13Al-7.89V-4.97Fe</td>
<td>Ti-1.07Al-12.51V-8.88Fe</td>
<td>Ti-2.84Al-1.53V-0.52Fe</td>
<td></td>
</tr>
<tr>
<td>σc / fm²</td>
<td>76.228</td>
<td>45.175</td>
<td>108.264</td>
</tr>
<tr>
<td>Correction Factor</td>
<td>1.0</td>
<td>0.593</td>
<td>1.420</td>
</tr>
</tbody>
</table>

Table 10: Corrected phase fractions for the neutron data in comparison with the synchrotron data at a heating rate of 5 K/min

<table>
<thead>
<tr>
<th></th>
<th>Synchrotron (822 K)</th>
<th>Neutron (828 K)</th>
<th>Neutron (827 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 K/min</td>
<td>33.4</td>
<td>37.4</td>
<td>36.0</td>
</tr>
<tr>
<td>20 K/min</td>
<td>66.4</td>
<td>62.6</td>
<td>64.0</td>
</tr>
<tr>
<td>20 K/min + Iso</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It was shown that a high density of ω-precipitates leads to earlier α¨-phase transition. A heating rate of 100 K/min prevents an ωinc-phase transition in detectable amounts so that the subsequent α¨-phase precipitation is postponed to 823 K as opposed to less than 700 K for all other heating rates. Heating rates of 5 K/min or less or an isothermal holding step at 623 K lead to a completely transitioned ω-phase, which
partakes in the subsequent β- to α”-phase transition. The ω-phase transforms back into β-phase before the α”-phase is formed, which is the likely cause of the slower (α”+α)-phase growth in experiments enabling an ideal ω-phase transition. The ideal ω-phase can form through extended diffusion and is therefore more depleted in β-stabilisers, which slows down the reverse transformation of ω- to β-phase. Fe depletion of the ideal ω-, α” and α-phases effect the neutron scattering amplitudes of the respective phase and thus the recorded intensities. As a result the Fe enriched β-phase fraction is about 15 mass-% lower in magnitude than that determined by high energy X-ray analysis, which is not affected by this phenomenon, because of the difference in diffraction mechanism. The influence of the alloying element distribution on the lattice parameters and the most likely phase transition sequence will be discussed in Section 6.3.4.

6.3.4 Analysis of the Lattice Parameter Evolution and the Structural Changes based on Rietveld Refinement

Rietveld analysis can help to distinguish the influence on lattice parameters due to concurrent effects of thermal expansion, structural change and variation in element distribution. To enhance understanding of the structural interrelation between phases and to conclude the lattice parameter dependencies it is useful to look at their geometric relations first. The geometric relation between β- and ω-phase is shown in Figure 124. On the left of the figure is the bcc unit cell placed on a corner. The middle shows the bcc structure in the hexagonal setup, which enables direct visualisation of required structural changes to form the ideal ω-phase on the right. It follows that the lattice parameters are interrelated by Equation (34).
The geometric relations between β- and ω-phase are shown in Figure 124. The left of the figure shows four bcc unit cells, where the filled atoms are highlighting the orthorhombic setup of the α”-phase that sits in the centre on an edge. In a similar manner on the right is the hexagonal α-phase with filled atoms showing the orthorhombic unit cell. The geometric relations are leading to the lattice parameter interrelations as given by Equation (34).

\[ a_\omega = \sqrt{2} a_\beta \]

\[ c_\omega = \frac{\sqrt{3}}{2} a_\beta \]

Figure 125: Orthorhombic setup of the bcc (left) and hcp (right) structures. (Duerig et al. 1982).
\[ a_\beta = a_{\alpha''} = a_\alpha \]
\[ \sqrt{2} a_\beta = b_{\alpha''} = \sqrt{3} a_\alpha \]
\[ \sqrt{2} a_\beta = c_{\alpha''} = c_\alpha \]

From these relations it is deducted that, \( \alpha'' \)- and \( \omega \)-phase would be related by Equation (36).

\[ a_\omega = c_{\alpha''} \]
\[ c_\omega = \frac{\sqrt{a_{\alpha''}^2 + c_{\alpha''}^2}}{2} \]

These geometric relations between \( \beta \)-, \( \alpha \)- and \( \alpha'' \)-phase dictate the atomic positions shown in Table 11. The second and fourth atomic positions of the \( \alpha'' \)-phase are affected by a factor – \( y \). \( Y \) determines the extent to which atomic positions of the \( \alpha'' \)-phase are closer to the \( \beta \)- or \( \alpha \)-phase. Thus, the degree of atomic shuffling to complete the \( \beta \)- to \( \alpha \)-phase transition lies between \( y = 1/4 \) for \( \beta \)-positions and \( y = 1/6 \) for \( \alpha \)-positions.

Table 11: Atomic positions for the \( \alpha \)-, \( \beta \)- and \( \alpha'' \)-phase

<table>
<thead>
<tr>
<th>Phase</th>
<th>Atomic positions as X, Y, Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \beta )</td>
<td>0, 0, 0</td>
</tr>
<tr>
<td>( \alpha'' )</td>
<td>0, 0, 0</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>0, 0, 0</td>
</tr>
</tbody>
</table>

The synchrotron experiment detailed in Section 6.1.2.1 in which the sample was heated at 5 K/min to 823 K was analysed by Rietveld refinement. The Rietveld method determines atomic positions among other parameters. From these positions \( y \) has been determined and is plotted as a function of temperature against the nominal values for atomic positions of the \( \alpha \)- and \( \beta \)-phase in Figure 126. Below a temperature of 734 K, \( y \) varies in magnitude and possesses values up to 0.191 which agrees with \( y \)-values measured by Barriobero-Vila et al. (2015a) for a Ti-5Al-5Mo-5V-
3Cr-1Zr alloy during similar heat treatments. Above 742 K, y lies on or very close to atomic positions of the α-phase (0.1667). 734 K coincides with the approximate temperature of disappearance of the ω-phase, which indicates an effect of ω-phase on atomic positions in the α”-phase. Substitutional elements also affect atomic positions and since the α”-phase nucleates quickly below 734 K, the variation of y from the positions near the α-structure suggests that the initial α”-precipitates are enriched in solute compared to the equilibrium condition. From temperatures above 734 K, y lies very close to its expected value for atomic positions in the α-phase and since the increase in the α”-phase fraction slows down significantly at these temperatures, it may be assumed that the growth of α”-precipitates occurs at the same rate as the diffusional processes at the these temperatures so that the alloying element content remains close to the equilibrium values.

Figure 126: y-factors for the α”-phase plotted against temperature. The values of the y-factors for atom positions in the β- and α-phase are also shown.

The Rietveld refinement for specimens subjected to a heating rate of 5 K/min also allows the determination of the lattice parameter evolution for all phases present as shown in Figure 127. The graph shows the lattice parameters resulting from the fit as dots while the interrelation of the lattice parameters following the geometric relations in Equations (34), (35) and (36) are shown as squares. This low heating rate allows for intermediate precipitation of both ω- and α”-phases before a stable α-phase is precipitated (compare Figure 121). The lattice parameter of the β-phase, $a_\beta$, remains relatively constant on this scale throughout the experiment (and will be discussed in more detail below), whereas the lattice parameters of the ω-phase, $a_\omega$ and $c_\omega$, show small changes in the first half of their stability range before remaining...
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relatively constant up to the disappearance of the ω-phase. On the other hand, the lattice parameters for the α- and α’’-phase alternate strongly just after their formation before reaching a relatively constant state.

Figure 127: Lattice parameter evolution from high energy X-ray data during continuous heating at a rate of 5 K/min to 823 K

A more detailed analysis of the β-lattice parameter development related to the phase transitions is shown in Figure 125. The temperature dependency of aβ is extrapolated up to about 550 K (before ω-precipitation initiates) and this linear thermal expansion is approximated by Equation (37). The change of the β-lattice parameter with temperature is described well by its linear extrapolation. The correlation coefficient, which determines the variation of the extrapolation from the data is equal to 0.95 up to 550 K. At temperatures above 550 K a linear approximation is insufficient in
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Describing the change in $a_\beta$ with temperature. Just before the $\beta$- to $\omega$-phase transition occurs at about 550 K, $a_\beta$ is equal to 3.246 Å, but decreases to 3.243 Å when the maximum amount of $\omega$-phase has precipitated at about 650 K. It was shown in Section 3.1.2 (Figure 14) that the alloying elements V and Fe reduce the lattice parameter of the $\beta$-phase and hence, this decrease in $a_\beta$ is most probably related to the growth of $\omega$-precipitates and the concomitant diffusion of $\beta$-stabilisers into the surrounding $\beta$-matrix. This increase in V and Fe in the matrix lowers the $\beta$-lattice parameter to the extent that the increase due to thermal expansion is overridden. These findings confirm previous observations on a correlation between $\omega$-precipitation and elemental partitioning following from the composition maps gathered in the TEM presented in Section 6.2.1 and 6.2.2. In the temperature range 650 to 700 K, the $\omega$-phase transforms back into $\beta$-phase and $\alpha''$-phase formation begins, which is accompanied by an increase in $a_\beta$ to 3.249 Å. This observation is consistent with the premise that solute lean $\omega$-regions dissolve in the $\beta$-matrix. The $\omega$-phase disappears at 725 K and $a_\beta$ decreases to a value of 3.242 Å at 823 K. This decrease in $a_\beta$ is attributed to the diffusion of $\beta$-stabilisers from the growing $\alpha$- and $\alpha''$-precipitates into the surrounding $\beta$-matrix. These findings provide evidence of the hypothesis that the $\alpha''$-phase is formed from the $\beta$-phase rather than directly from the $\omega$-phase. The change in $a_\beta$ caused by solute diffusion will be discussed further at the end of this Section with the aid of Vegard’s law.
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Figure 128: Change in lattice parameter $a_\beta$ as a function of temperature at a heating rate of 5 K/min

$$a_\beta = 0.000046 \times \frac{T}{K} + 3.2205 \text{Å} \quad (37)$$

Figure 127 shows that the $\alpha''$-phase nucleates with lattice parameters approximating those of the $\beta$-phase in an orthorhombic setup (Equation (35)) and comparatively far from values expected for a formation from the $\omega$-phase (Equation (36)). At 696 K $c_\alpha''$ is 4.585 Å, which is close to 4.594 Å for $\sqrt{2}a_\beta$ and rather far from the value of $a_\omega$ of 4.635 Å. These observations support the finding that the $\omega$-phase transforms back to $\beta$-phase before $\alpha''$-phase is formed from the $\beta$-phase. All three $\alpha''$-phase lattice parameters alternate strongly up to 742 K when the lattice parameters are approximating values of the $\alpha$-phase in an orthorhombic setup (Equation (35)). This observation suggests that $\alpha''$-phase forms from $\beta$-phase and can be regarded as a transition step to the following $\alpha$-precipitation. The drastic changes of the $\alpha''$-phase lattice parameters between 696 and 742 K can most likely be attributed to two major causes. Firstly, the $\alpha''$-phase nucleation occurs with a composition not at equilibrium and the following diffusion of $\beta$-stabilisers into the $\beta$-matrix contributes to the observed changes in lattice parameters. The second cause affecting the lattice parameters are dislocations created in the phase boundary regions of the $\alpha''$-phase, which are required to enable the fit into the $\beta$-matrix. This phase boundary region
would be relatively large for small $\alpha''$-precipitates. Through the growth of $\alpha''$-precipitates the relative amount of these highly distorted $\alpha''$-phase regions is reduced and the overall lattice parameters change.

In order to further explore the mechanisms of phase changes in this alloy system, the lattice parameter evolution as a function of temperature was experimentally determined at a heating rate of 20 K/min in a neutron diffraction experiment described in Section 6.1.3.2. This higher heating rate prevents a $\beta$- to ideal $\omega$-phase transition so that $\omega_{\text{inc}}$- and $\alpha''$-phase are precipitated before a stable $\alpha$-phase is formed (compare Figure 122). The lattice parameters of each phase as a function of temperature are shown in Figure 129.

At temperatures above 600 K the structural proximity of the incompletely transitioned $\omega$-phase to the $\beta$-phase can be observed. As correlated in Equation (34) the values for $a_\omega$ are approaching $\sqrt{2} a_\beta$ (4.683 and 4.589 Å at 607 K respectively) while $c_\omega$ can be seen to possess very similar values to $\sqrt{3}/2 a_\beta$ (2.795 and 2.81 Å respectively). This trend continues up to the disappearance of $\omega_{\text{inc}}$-phase after 653 K, thus indicating the reverse transition of $\omega_{\text{inc}}$-phase to $\beta$-phase. The lattice parameter evolution of the $\alpha''$- and $\alpha$-phase is similar to the findings at a heating rate of 5 K/min discussed with reference to Figure 127. The $\alpha''$-phase is nucleating at 676 K with a $c_\alpha$ of 4.664 Å at a $\sqrt{2} a_\beta$ of 4.589 Å and grows to approach lattice parameter values resembling an orthorhombic setup of the $\alpha$-phase at 765 K ($c_\alpha$ of 4.693 Å and $c_\alpha$ of 4.672 Å) as given in Equation (35). These observations confirm the $\alpha''$-phase as a transition step to $\alpha$-phase formation. Furthermore, the observed changes in $\alpha''$-phase lattice parameters indicate the structural and compositional evolution during the precipitate growth stage towards the equilibrium $\alpha$-phase.
Figure 129: Lattice parameter evolution from neutron data during continuous heating at a rate of 20 K/min to 823 K

In an attempt to further elucidate the mechanisms by which the ω-, α”- and α-phases evolve, the lattice parameter of the β-phase is plotted as a function of temperature separately in Figure 130. The change in lattice parameter of the β-phase as a result of thermal expansion can be approximated by Equation (38) with a correlation coefficient of 0.99. The improved fit for the neutron diffraction experiment is due to improved grain statistics because of the use of large specimens. In comparison with the phase evolution data for this experiment shown in Figure 120 it follows that aαβ is stagnating during the ω-phase transition implying that the alloying elements diffused less than at a heating rate of 5 K/min (Figure 128) and provides evidence that the extant of the {111}β plane collapse is related to the degree of diffusion. From 680 K
on the nucleation and growth of \((\alpha''+\alpha)\)-phase leads to extensive diffusion of \(\beta\)-stabilisers into the matrix and thus a significant drop in the value of \(a_\beta\).

![Graph showing lattice parameter evolution](image)

**Figure 130:** Change in lattice parameter \(a_\beta\) as a function of temperature at a heating rate of 20 K/min

\[
a_\beta = 0.000059\, \text{Å} \times \frac{T}{K} + 3.2135\, \text{Å}
\]  

(38)

Finally, the lattice parameter evolution shown in Figure 131 for the neutron experiment following at a heating rate of 20 K/min, but including an additional holding step at 623 K will be discussed. The evolution of the \(\alpha''\)- and \(\alpha\)-lattice parameters is comparable to the results for a low heating rate presented in Figure 127. The \(\alpha''\)-phase is approaching the crystal structure of the \(\alpha\)-phase at 823 K. So that \(b_{\alpha''}\) and \(c_{\alpha''}\) have almost the same value as their equivalent parameters \(\sqrt{3}a_\alpha\) and \(c_\alpha\) and only \(a_{\alpha''}\) shows small variations. The lattice parameter of the \(\beta\)-phase will be discussed with reference to Figure 131.
Figure 131: Lattice parameter evolution from neutron data during heating at a rate of 20 K/min to 623 K, holding for 70 min and continued heating at a rate of 20 K/min to 823 K.

The approximation of the linear thermal expansion of $a_\beta$ given in Equation (39) was determined for a heating rate of 20 K/min for the neutron diffraction experiment including the $\omega$-ageing step at 623 K. The linear thermal expansion is reasonably close to that for a continuous heating experiment at a rate of 20 K/min. However, the approximation given in Equation (39) has a correlation coefficient of only 0.94. Thermal expansion accounts for the change in $a_\beta$ up to a temperature of 500K. The $\omega_{inc}$-phase forms between 500 K and 623 K, but the transition is not completed most probably due to the low diffusion rates of the alloying elements. However, the diffusion rates are high enough to negate the effect of linear thermal expansion so that $a_\beta$ remains constant (3.25 Å). During holding at 623 K the phase transition is
completed along with a redistribution of alloying elements which leads to the enrichment of the β-phase in V and Fe, thus decreasing its lattice parameter by 0.05 Å. This observation confirms that the degree of diffusion enabled through the holding step at 623 K is sufficient to allow for a full β- to ideal ω-phase transition, which presents the major difference as compared to continuously heating at a rate of 20 K/min. Between 623 K and 650 K the β-phase fraction slightly increases and the dissolution of ω-precipitates into the β-matrix leads to an increase in $a_β$ due to the concomitant dilution of β-stabilisers. This maximum in $a_β$ at 685 K is followed by a slow drop up to 710 K due to the parallel onset of the $α''$-phase transition, which is occurring with another redistribution of Fe and V. Between 710 and 745 K the $α''$-phase fraction increases rapidly, leading to further enrichment of V and Fe in the β-phase and therefore lowering the lattice parameter $a_β$. Thereafter, the growth rate of the ($α''+α$)-phase is reduced.

![Graph showing the change in lattice parameter $a_β$ as a function of temperature](image)

Figure 132: Change in lattice parameter $a_β$ as a function of temperature at a heating rate of 20 K/min with an isothermal holding step at 623 K for ~70 min

$$a_β = 0.000056\,\text{Å} \times \frac{T}{K} + 3.2232\,\text{Å}$$  \hspace{1cm} (39)

As discussed, the theoretical increase of the β-lattice parameter due to thermal expansion deviates from $a_β$ determined from diffraction data because of the enrichment of the β-phase with β-stabilisers following the β- to ω- and β- to $α$-phase
transitions. Vegard’s law (Vegard 1921) as given in Equation (40) shall be used to
determine the combined effects of thermal expansion and solute content on the
lattice parameter of the β-phase. By combining the thermal expansion at the known
alloy composition of Ti-1.13Al-7.89V-4.97Fe (in mass-%, compare Table 6) with the
changes in solute content of the β-phase at 823 K (Ti-1.07Al-12.51V-8.88Fe (in mass-
%)) determined from the linescan shown in Figure 83 the actual β-lattice parameter
is calculated. Al was excluded from calculations, because it is not a β-stabiliser and
also its influence would be negligible due to the very minor change in composition
that was determined. The values for the $a_i$ and $x_i$ at 823 K are given in Table 12, where
$a_{Ti}$ was calculated for its known composition of Ti-1.13Al-7.89V-4.97Fe (mass-%)
under applying Equation (38). The atomic fractions for V and Fe at 823 K used in
Vegard’s law had to be adjusted according to the difference to the new composition
1.07Al-12.51V-8.88Fe (mass-%).

$$a_\beta = a_{Ti} \times x_{Ti} + a_V \times x_V + a_{Fe} \times x_{Fe}$$

(40)

Table 12: Lattice parameters and atomic fraction for Ti-1.13Al-7.89V-4.97Fe, V and Fe

<table>
<thead>
<tr>
<th>Ti-1.13Al-7.89V-4.97Fe</th>
<th>V</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>a / Å</td>
<td>x</td>
<td>a / Å</td>
</tr>
<tr>
<td>3.2625</td>
<td>0.9207</td>
<td>3.024</td>
</tr>
</tbody>
</table>

Thus, the β-lattice parameter at 823 K for a heating rate of 20 K/min corrected for
the change in compositions is 3.2382 Å, which lies 0.0244 Å below the value that only
considered thermal expansion. Table 13 is listing the lattice parameters only
considering thermal expansion, those corrected for composition by subtracting
0.0244 Å and the lattice parameters determined from diffraction for the different
heat treatments. The lattice parameters from Rietveld fitting are very close to the
values corrected for composition. Therefore, it is confirmed that the alterations in $a_\beta$
following the β- to ω- and β- to α-phase transformations are mainly caused by the
change in composition due to the solute enrichment of the β-phase.
Table 13: β-lattice parameters determined for thermal expansion, thermal expansion + composition changes and from Rietveld refinement for the different heat treatments

<table>
<thead>
<tr>
<th></th>
<th>( a_\beta / \text{Å} )</th>
<th>( a_\beta / \text{Å} )</th>
<th>( a_\beta / \text{Å} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Thermal</td>
<td>Thermal + Comp.</td>
<td>Rietveld</td>
</tr>
<tr>
<td>5 K/min High en. X-rays</td>
<td>3.2581</td>
<td>3.2337</td>
<td>3.2416</td>
</tr>
<tr>
<td></td>
<td>(822 K)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 K/min Neutrons</td>
<td>3.2625</td>
<td>3.2382</td>
<td>3.2352</td>
</tr>
<tr>
<td></td>
<td>(828 K)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 K/min + (Iso: 623K) Neutrons</td>
<td>3.2690</td>
<td>3.2446</td>
<td>3.2394</td>
</tr>
<tr>
<td></td>
<td>(827 K)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

6.3.4.1 Lattice Strains Following from the Phase Transformations

The lattice parameter development and the correlations given in Equation (34) enable the calculation of lattice strains due to the \( \omega \)-precipitation as given in Equation (41).

\[
\varepsilon_{a_\omega} = \frac{a_\omega - \sqrt{2}a_\beta}{\sqrt{2}a_\beta} \times 100\%
\]

\[
\varepsilon_{c_\omega} = \frac{c_\omega - \sqrt{3}/2a_\beta}{\sqrt{3}/2a_\beta} \times 100\%
\]

(41)

The formation of \( \omega \)-phase under a heating rate of 5 K/min occurs with an \( \omega \)-phase lattice parameter, \( a_\omega \), of 4.704 Å compared to 4.590 Å for \( \sqrt{2}a_\beta \) and thus leads to a lattice strain of 2.48 %. On the other hand \( c_\omega \) equals 2.775 Å, which is slightly below the value of \( \sqrt{3}/2a_\beta \) of 2.811 Å at 563 K, resulting in a lattice strain of -1.28%. When the temperature is increased by ~70 K, \( \omega \)-precipitates are growing and stabilising with
Results and Discussion

respect to the matrix through diffusion of alloying elements into the $\beta$-matrix. This results in opposing changes for $a_\omega$ and $c_\omega$ with an $a_\omega$ of 4.643 Å compared to 4.586 Å for $\sqrt{2}a_\beta$ and $c_\omega$ equalling 2.848 Å (slightly higher than $\sqrt{3}/2a_\beta$ of 2.808 Å) thereby reducing the lattice strains to 1.24 % and 1.42 % respectively. These findings correlate well with the outcomes of the electron microscopy investigation (see Figure 67 (Section 6.2.1)). In this investigation a mismatch of 0.6˚ to 1˚ was found between the $<001>_\omega$ and $<111>_\beta$ directions for $\omega$-precipitates embedded in the $\beta$-matrix, which is an indication that lattice strains result from early $\omega$-precipitation. More developed $\omega$-precipitates (Section 6.2.2) did not show any detectable mismatch, but it is possible that the measurement of very low lattice strains is beyond the limit of detectability. Also the HRSTEM investigation was done from $<110>_\beta$ so that only lattice strains in certain directions can be determined.

In comparison, neutron diffraction results for a heating rate of 20 K/min including an additional holding step at 623 K confirmed the synchrotron results. Here, the lattice strains between $a_\omega$ and $\sqrt{2}a_\beta$ and $c_\omega$ and $\sqrt{3}/2a_\beta$ are on average 1.11 % and 1.37 %.

The benefit in nucleating $\alpha''$-phase, which later transforms into $\alpha$-phase, instead of a direct $\beta$- to $\alpha$-phase transformation, becomes clear when comparing the required lattice strains for the formation of $\alpha''$-phase compared to the strains required for $\alpha$-formation. The lattice strains can be calculated from the lattice parameter relations in Equation (35) as given in Equation (42).

\[
\varepsilon_{a\alpha''} = \frac{a_{\alpha''} - a_\beta}{a_\beta} \times 100\% \\
\varepsilon_{b\alpha''} = \frac{b_{\alpha''} - \sqrt{2}a_\beta}{\sqrt{2}a_\beta} \times 100\%
\]

\[
\varepsilon_{c\alpha''} = \frac{c_{\alpha''} - \sqrt{2}a_\beta}{\sqrt{2}a_\beta} \times 100\%
\]

\[
\varepsilon_{a\alpha} = \frac{a_{\alpha} - a_\beta}{a_\beta} \times 100\% \\
\varepsilon_{b\alpha} = \frac{\sqrt{3}a_{\alpha} - \sqrt{2}a_\beta}{\sqrt{2}a_\beta} \times 100\%
\]

\[
\varepsilon_{c\alpha} = \frac{c_{\alpha} - \sqrt{2}a_\beta}{\sqrt{2}a_\beta} \times 100\%
\]  

The lattice strains originating from the nucleating $\alpha''$-phase thus calculated at 696 K are $\varepsilon_{a\alpha''} = -7.53 \%$, $\varepsilon_{b\alpha''} = 8.49 \%$ and $\varepsilon_{c\alpha''} = -0.21 \%$. By comparison, the lattice strains resulting from $\alpha$-nucleation at 750 K are $\varepsilon_{a\alpha} = -8.55 \%$, $\varepsilon_{b\alpha} = 12.01 \%$ and $\varepsilon_{c\alpha} =$
2.66%. Hence, it is clear that α″-formation is energetically more favourable since a reduction in lattice strains up to ~3.5% can be achieved. In their study on the martensitic α″-phase transformation in Ti-10V-2Fe-3Al Duerig et al. (1982) and Barriobero-Vila et al. (2015b) have shown that the magnitude of these calculated strains are reasonable. The lattice parameters determined for the sample heated at a rate of 100 K/min to 823 K are different from the values at a heating rate of 5 K/min. The α″-phase nucleated after holding for 30 s at 823 K with \(a_\alpha = 2.98\) Å, \(b_\alpha = 5.10\) Å and \(c_\alpha = 4.72\) Å. These values are similar to those determined at 5 K/min heating rate for an α″-structure very close to the orthorhombic setup of the equilibrium α-phase. The β-phase possesses a lattice parameter of 3.240 Å. So that the lattice strains originating from the α″-nucleation at a heating rate of 100 K/min can be determined to be \(\varepsilon_{a\alpha″} = -8.02\%\), \(\varepsilon_{b\alpha″} = 11.30\%\) and \(\varepsilon_{c\alpha″} = 3.01\%\). As can be seen they are very close to values measured for nucleating α-phase obtained at a slow heating rate of 5 K/min. Hence, indicating the comparatively higher drive for α″-formation due to the instability of the β-matrix at these temperatures. Another reason for a higher α″-nucleation energy at this heating rate is the lack of the preliminary ω-precipitation which would have served as nucleation spots and thus accelerated the α-phase transformation kinetics. It also shows that the necessity for an intermediate α″-phase transformation is reduced with increasing heating rate. So that a further increase in heating rate might lead to the disappearance of an intermediate α″-phase transition.

The comparison of these results with the neutron diffraction data for a heating rate of 20 K/min, including the ω-ageing step at 623 K show that lattice strains are of a similar order as in the synchrotron experiment with a heating rate of 5 K/min. The lattice strains originating from the nucleating α″-phase have been calculated at 709 K as \(\varepsilon_{a\alpha″} = -9.06\%\), \(\varepsilon_{b\alpha″} = 8.88\%\) and \(\varepsilon_{c\alpha″} = 1.81\%\). Whereas the lattice strains resulting from α-phase nucleation at 745 K are \(\varepsilon_{a\alpha} = -10.06\%\), \(\varepsilon_{b\alpha} = 10.15\%\) and \(\varepsilon_{c\alpha} = 2.85\%\). Hence, it can be confirmed that α″-formation is energetically favourable due to up to ~1.3 % reduction in lattice strains required for its formation.
Conclusions

7 Conclusions

In-situ high-energy X-ray, neutron and electron diffraction studies along with high-resolution electron microscopy provided new insights into the sequence of and the mechanisms by which phase transformations occur in a near-β Ti-1Al-8V-5Fe alloy.

The fraction formed and the stability range of intermediate phases such as the ω-phase are determined in large measure by the rate and extent of solute element diffusion.

Solute element diffusion also plays a pivotal role in determining α-nucleation kinetics and hence, the homogeneity and morphology of α-phase precipitation.

Because the rate of diffusion of the alloying elements play such an important role, microstructural development in the Ti-1Al-8V-5Fe alloy can be manipulated by heat treatment.

Heating rates of up to 5 K/min allow for sufficient alloying element diffusion to enable an intermediate β- to ideal ω-phase transition.

On approaching the temperature where the α”-phase would be stable, the β-phase transforms directly into the α”-phase and the ω-phase transforms back into β-phase.

Following the β- to α”-phase transition, the α-phase is formed, as it represents the equilibrium phase at a temperature of 823 K. The intermediate phase transition β- to α”-phase, which occurs prior to α-phase nucleation, is driven by a reduction in lattice strain (up to 3.5 %).

An increase in heating rate leads to all the phase transitions occurring at higher temperatures.

At high heating rates the transformation of the ω-phase into its ideal structure is inhibited unless sufficient time is allowed for the diffusion of alloying elements by including a holding step in the heat treatment cycle (623 K in the present study).

Transition electron microscopy revealed that the quenched β-phase contains incompletely transitioned ωₙₙ nuclei which, upon heating will lead to an increase in the fraction of the ω-phase.
Conclusions

The initial growth of $\omega_a$-nuclei to form precipitates featuring incomplete \{111\}_\beta plane collapse is less dependent on heating rate, and therefore diffusion, than continued collapse. Hence, in this study heating rates lower than 5 K/min (or alternatively continued holding at $\omega$-ageing temperatures of about 623 K) led to complete transformation of $\beta$ to ideal $\omega$-phase, which in turn resulted a homogeneous distribution of $\omega$-precipitates in the $\beta$-matrix. In contrast, a heating rate of 20 K/min led to a homogeneous distribution of incompletely transitioned $\omega$-precipitates in the $\beta$-matrix and hence, it follows that diffusion of alloying elements play an important role in the extent of the \{111\}_\beta plane collapse.

Convincing experimental evidence has been provided in support of the premise that the $\beta$- to $\omega$-phase transition occurs through a continuous repetition of two steps: partial \{111\}_\beta plane collapse and diffusion of alloying elements until the $\omega$-phase reaches its stable hexagonal crystal structure.

The presence of $\omega$-phase precipitates has a determining influence on the nucleation of the $\alpha''$- and $\alpha$-phases and the density of $\omega$-precipitates plays a more important role in enhancing $\alpha''$- and $\alpha$-phase formation than the degree of \{111\}_\beta plane collapse within those precipitates. In practical terms this means that a microstructure consisting of small, homogeneously distributed $\alpha$-precipitates can be achieved by continuous heating at rates of up to 20 K/min to the final ageing temperature (or at higher rates but then by including an isothermal holding step at $\omega$-ageing temperatures of about 623 K).

When fully transformed $\omega$-precipitates (with a hexagonal crystal structure) act as nuclei for $\alpha$-phase formation, the $\alpha$-phase so formed has a composition closer to equilibrium than when the $\alpha$-phase nucleates on incompletely transitioned $\omega$-precipitates. This observation implies that $\alpha$-precipitates grow into regions of existing $\omega$-precipitates and hence, $\alpha$-nucleation and growth kinetics are improved by the reduced solute content in these regions, which increases the thermodynamic driving force for $\alpha$-phase formation. Hence, $\alpha$-phase nucleation kinetics are enhanced by the presence of a high density of $\omega$-precipitates.

In the absence of a high density of $\omega$-precipitates $\alpha$-phase precipitation occurs at higher temperatures and/or longer holding times, resulting in the formation of few,
Conclusions

Coarse primary α-precipitates. Smaller secondary α-precipitates eventually nucleate on the primary precipitates, but this precipitation sequence leads to an inhomogeneous microstructure.

The new insights provided by the present study set the basis for the design of thermo-mechanical processing routes of the Ti-1Al-8V-5Fe alloy.

The new findings with respect to the influence of the ω-phase on α-phase nucleation, growth, morphology and distribution provides a means of tailoring the mechanical properties of this near-β titanium alloy.
8 Outlook

Conclusions drawn from this study provide promising perspectives for future work using \textit{in-situ} diffraction techniques in combination with transmission electron microscopy to experimentally explore the detailed mechanisms of phase transformations. The insights on the influence of ω-precipitation on α-phase nucleation kinetics, morphology and distribution provide the basis for the design of thermo-mechanical processing routes of the Ti-1Al-8V-5Fe alloy. By furthering research regarding textural changes of phases as influenced by the processing parameters and combining them with already conducted studies on microstructures of near-β titanium alloys and the mechanical properties they possess, it will become possible to tailor and predict final properties of this near-β titanium alloy.

The diffusion of alloying elements was identified as a determining factor for the fraction formed and the stability range of intermediate phases such as the ω-phase. Also, solute element diffusion is a major factor in determining α-nucleation kinetics and hence, the homogeneity and morphology of α-phase precipitation. Therefore the findings from this research are also useful to answer open questions in other systems with similar solute type and content, such as Ti-10V-2Fe-3Al. However, systems such as Ti-Mo would need to be investigated separately due to the strong difference in diffusion rates of Mo and Fe, which would affect and possibly change the phase transformation mechanisms.
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Figure 133: Full Debye Scherrer rings collected after heating to 1173 K and fast cooling to room temperature

Figure 134: Full Debye Scherrer rings collected during heating at a rate of 5 K/min at 643 K
Figure 135: Full Debye Scherrer rings collected during heating at a rate of 5 K/min at 717 K

Figure 136: Full Debye Scherrer rings collected during heating at a rate of 5 K/min at 823 K
Figure 137: Synchrotron powder diffraction pattern at 1173 K (red) and following cooling at 298 K (green)

Figure 138: Full Debye Scherrer rings collected after heating to 1173 K and fast cooling to room temperature
Figure 139: Full Debye Scherrer rings collected during heating at a rate of 100 K/min at 643 K

Figure 140: Full Debye Scherrer rings collected during heating at a rate of 100 K/min at 716 K
Figure 141: Full Debye Scherrer rings collected during heating at a rate of 100 K/min at 823 K