Strengthening of metastable beta titanium alloys

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This dissertation is submitted for the degree of

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I would like to dedicate this thesis to my wife, to my sister and to my parents.
Declaration

I hereby declare that except where specific reference is made to the work of others, the contents of this dissertation are original and have not been submitted in whole or in part for consideration for any other degree or qualification in this, or any other university. This dissertation is my own work and contains nothing which is the outcome of work done in collaboration with others, except as specified in the text and Acknowledgements. This dissertation contains fewer than 65,000 words including appendices, bibliography, footnotes, tables and equations and has fewer than 150 figures.

The following papers have been published:


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Abstract

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Using current technology, it is now possible to probe material at atomic length scales, increasing our fundamental understanding of material behaviour and properties. Metastable \( \beta \) titanium alloys are a subset of titanium alloys with huge potential for the aerospace sector. However, they exhibit atomic transformations which, even after 60 years of research, are still disputed. For example, these alloys are strengthened using the \( \omega \) phase, but the mechanism by which this phase forms and its stability are still in question. The aim of this PhD project was to investigate the strengthening of metastable Ti-15 wt.%Mo by understanding the stability and transformation pathways which make the metastable \( \beta \) titanium alloy class unique.

Athermal \( \omega \) shares the same composition as the \( \beta \) matrix and is formed by rapid cooling from the \( \beta \) phase field. The classical theory of athermal \( \omega \) formation is based upon a diffusion-less mechanism in which consecutive pairs of \( \{111\}_\beta \) planes collapse together. However, latest high-resolution electron microscope observations have suggested chemical alterations occur as well, which give reason to challenge this classical formation mechanism.

Two novel methods were explored to determine the nature of the \( \omega \) phase: 1) electron imaging of thin material at different collection angles and 2) total X-ray scattering analysis of large volumes of material. Complementary techniques are invaluable since thin foil artefacts were identified. In particular, a new B2 structured phase in the Ti-15 wt.%Mo alloy was observed only in thin electron transparent material.

Experimental data from the two new methods were compared to simulations. It was found that a frozen phonon description of the \( \omega \) structure provided a best fit in both scenarios. The results are therefore consistent with the classical theory of \( \omega \) formation but the collapse of the \( \{111\}_\beta \) planes towards the \( \omega \) phase is not considered complete.
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Chapter 1

Introduction

Adding value to a material by improving characteristics that influence operating efficiency, safety and cost is a central part of Materials Science and Engineering. A key objective is to ascertain how a material can be tailored to meet a niche application. Using current technology, it is now possible to probe material at atomic length scales, increasing our fundamental understanding of material behaviour and properties. Within certain sectors, such as aerospace and medicine, improving the safety of a material can justify an increase in cost [1]. Metastable beta ($\beta$) titanium (Ti) alloys are a subset of titanium alloys with huge potential for adding value in these sectors. However, they exhibit atomic transformations which, even after 60 years of research, are still disputed. For example, these alloys are strengthened using the omega ($\omega$) phase, but the mechanism by which this phase forms and its stability are still in question [2]. Within the aerospace industry in particular, knowledge of the strengthening behaviour in metastable $\beta$ alloys is critical for integration into future generations of jet engines. The aim of this PhD project was to investigate the strengthening of metastable $\beta$ titanium alloys for this purpose, through understanding the stability and transformation pathways which make the metastable $\beta$ titanium alloy class unique.

In general, $\beta$ alloys are the class of titanium alloys with enough element additions to retain the body centred cubic (BCC) beta matrix at room temperature. Typically, these additions are transition metals such as molybdenum (Mo), vanadium (V), chromium (Cr), iron (Fe) and niobium (Nb). The total strength of these alloys is the sum of several strengthening mechanisms and will vary between systems. However, a critical strengthening mechanism for all $\beta$ alloys is the precipitation of a second phase alongside the matrix $\beta$ phase, such as the equilibrium hexagonal close packed (HCP) alpha ($\alpha$) phase.
Metastable $\beta$ alloys, the focus of this project and literature review (Chapter 2), are defined by a composition range within which the $\beta$ phase can decompose to non-equilibrium phases. These metastable precipitates, such as the $\omega$ phase, are nominally a better strengthener than the equilibrium $\alpha$ phase. However, this improvement in strength can cause a significant reduction in ductility. As a result of this, early alloys were designed to suppress or avoid the $\omega$ phase [3].

Recent design ethos is to utilise the $\omega$ phase as a tool for microstructural refinement of the $\alpha$ phase and thereby balance strength and ductility. Consequently, optimal mechanical properties have been shown by a two-step process involving first the formation of the $\omega$ phase and then precipitation of the $\alpha$ phase at the expense of the $\omega$ phase. Through the two-step process, the $\alpha$ precipitates are significantly refined as they heterogeneously nucleate on the finely distributed $\omega$. Importantly, this two-step strategy requires a full understanding of phase stability and characterisation of the intermediary $\omega$ phase, which are currently disputed and are the topic of this work.

The non-equilibrium $\omega$ phase can be described as athermal or isothermal depending on the occurrence of long range diffusion and both can precipitate in metastable $\beta$ titanium alloys. Isothermal $\omega$ is compositionally distinct from the $\beta$ matrix and precipitates during low temperature ageing by a nucleation and growth model. The temperatures over which different phases occur, along with the respective compositions, are presented in Chapter 3.

In contrast to isothermal $\omega$, athermal $\omega$ shares the same composition as the $\beta$ matrix and is formed by rapid cooling from the $\beta$ phase field. The classical theory of athermal $\omega$ formation in metastable $\beta$ titanium alloys is based upon a diffusion-less mechanism in which consecutive pairs of $\{111\}_\beta$ planes collapse together [4]. However, latest high-resolution electron microscope observations have suggested chemical alterations occur as well, which give reason to challenge this classical formation mechanism [5, 6]. Whilst high angle annular dark field (HAADF) detectors can simultaneously image atomic structure and composition, the interaction between the electron beam and lattice softening is often not fully considered, leading to features that could be misinterpreted as local structure. This is addressed in Chapter 4.
Attention in the $\beta$ titanium community has also recently been drawn to transient phases observed during low temperature treatments [7]. Here in this project, a new structured phase was observed using *in situ* low temperature electron microscopy. These observations and associated analyses, reported in Chapter 5, highlight the importance of thin foil effects.

Lastly, in Chapter 6, in order to further investigate the athermal to isothermal transformation, a new application of the technique, *Total Scattering*, was employed on a titanium alloy [8]. Whilst this is the first time this has been applied to the study of the athermal to isothermal $\omega$ transformation, this technique could also have far reaching implications for understanding the local structure of engineering metals.
Chapter 2

Literature Review
2.1 \( \beta \) titanium alloys

Titanium, has several intrinsic properties, such as low density, which make it an attractive choice for aerospace applications [9]. Despite a high ore extraction cost, the advantages of using titanium outweigh other materials, particularly in the aerospace sector where the strength to weight ratio is critical. Specific strength, the ratio between strength and density \( \frac{\sigma}{\rho} \), is an alloy property which, amongst other figures-of-merit, is a key consideration for industrial applications. Metastable beta (\( \beta \)) titanium alloys are the strongest but also the densest when compared to other classes of titanium. Currently, \( \beta \) alloys are only used commercially in niche applications where factors such as safety are more important than specific strength, for example, in landing gear and critical corrosion resistant components on the Boeing and Airbus aircrafts [1, 9–11]. However, \( \beta \) alloys have the potential for further increases in strength, justifying the higher density and making specific strength an important consideration.

This chapter presents a review of \( \beta \) titanium alloys, their strengthening mechanisms and how improvements can be achieved. In particular, secondary phases have been shown to play a key role in defining the properties of \( \beta \) alloys [12, 13] but the precise nature, formation and transformation of the equilibrium and non-equilibrium phases are still largely unknown [14].

2.2 \( \beta \) titanium systems

Under ambient pressure, pure titanium exists in either the \( \alpha \) phase or the \( \beta \) phase depending on temperature. Above 882°C, also known as the allotropic temperature, the \( \beta \) phase is more stable than the \( \alpha \) phase. Therefore, material held at temperatures above the allotropic temperature will exist in the \( \beta \) phase. Cooling pure titanium from a high temperature to room temperature will cause a transformation back to the \( \alpha \) phase.

Titanium alloys are mixtures of titanium and other elements which can alter the temperature over which the \( \alpha \) and \( \beta \) phases are stable. This is because the alloying elements can stabilise the \( \alpha \) phase or the \( \beta \) phase. Key alloying elements which effect the \( \beta \) phase are generally transition metals (\( T_m \)) such as molybdenum (Mo), tantalum (Ta), niobium (Nb), tungsten (W), vanadium (V), chromium (Cr), nickel (Ni), manganese (Mn), cobalt (Co), iron (Fe), aluminium (Al), zirconium (Zr) and tin (Sn) [15]. However, nitrogen (N), oxygen (O) and hydrogen (H) impurities can also have a significant impact on phase stability [16–19].
ent transition metal additions will stabilise the $\beta$ phase by varying amounts. Historically, the abilities of the different elements to stabilise the $\beta$ phase have been compared against the stabilising effects of Mo. This normalisation is historical since the early $\beta$ alloys generally involved Mo additions [20]. The Mo equivalence of an alloy can be calculated using Equation 2.1 which shows the Mo equivalences for several common transition metal additions. A negative equivalence means the $\alpha$ phase is being promoted over the $\beta$ phase. Therefore, Mo, Ta, Nb, W, V, Cr, Ni, Mn, Co and Fe are $\beta$ stabilisers whereas Al, Zr, Sn and O are key $\alpha$ stabilisers.

\[
\text{Mo}_{\text{eq}} = [\text{Mo}] + \frac{[\text{Ta}]}{5} + \frac{[\text{Nb}]}{3.6} + \frac{[\text{W}]}{2.5} + \frac{[\text{V}]}{1.5} + 1.25[\text{Cr}] + 1.25[\text{Ni}] + 1.7[\text{Mn}] + 1.7[\text{Co}] + 2.5[\text{Fe}] - \frac{[\text{Al}]}{6} - \frac{[\text{Zr}]}{3} - 10[\text{O}]
\]

(2.1)

With sufficient $\beta$ stabilising additions, the $\beta$ phase can be retained at room temperature. In general terms, $\beta$ titanium alloys refer to a category of titanium alloys which contain a $\beta$ parent phase stabilised to room temperature and that exhibit exceptional strength. However, some additional sub-classifications can be made depending on the formation of non-equilibrium phases which compete with the equilibrium phases following addition of $\beta$ stabilisers. Figure 2.1 is a schematic representation of the effect of $\beta$ stabilising elements against temperature on phase stability [13, 21–23]. The phase boundaries drawn in bold are the equilibrium boundaries and are only drawn for temperatures above 200°C where diffusion is fast enough to reach equilibrium compositions within reasonable times. Different classes of titanium are indicated by the red arrows. At room temperature $\alpha$ alloys contain only the stable $\alpha$ phase, $\alpha$-$\beta$ alloys contain both $\alpha$ and $\beta$ phase, and stable $\beta$ alloys contain only the $\beta$ phase. The dotted line indicates the non-equilibrium martensite start temperature, $M_s$, for the martensite phases and the non-equilibrium omega ($\omega$) phase. The metastable $\beta$ alloys are the alloys which contain enough $\beta$ stabilising elements to suppress a martensite transformation but not enough to suppress $\omega$ phase formation. Typically, this is 10 wt.% in the Ti-Mo system [24]. Therefore, a 10 wt.%Mo equivalence is accepted in other alloys [25]. The metastable $\beta$ alloys are particularly intriguing as they can reach the highest strengths of all the classes of titanium [26–28].
Fig. 2.1 A generally accepted $\beta$-isomorphous pseudo-binary phase diagram with bold lines schematically showing the equilibrium phase boundaries. Different classes of titanium are indicated by the red arrows. The dotted line indicates the martensite start, $M_s$, below which a martensite transformation will occur.
2.3 Phases in \( \beta \) titanium alloys

All \( \beta \) alloys can retain the \( \beta \) phase at room temperature and all \( \beta \) stabilisers affect the relative stability of the \( \beta \) phase to the \( \alpha \) phase. However, the different \( \beta \) stabilising additions can also affect the number of equilibrium phases. Typical phase diagrams and solute additions are shown in Figure 2.2. In the simplest cases, the \( \beta \) stabilising additions suppress the \( \alpha \) phase and promote the \( \beta \) phase to such an extent that a mutual solubility across all compositions can be found. These additions are called \( \beta \) isomorphous additions. In contrast, other additions promote the formation of additional phases. These are called eutectoid formers as they promote a eutectoid transformation. One example of an intermetallic phase which can be found is an ordered B2 phase with a primitive CsCl structure. The B2 phase contains Pm-3m symmetry and can be regarded as BCC with different species at 0,0,0 to 1/2,1/2,1/2. Based on combinations of miscibility in the \( \alpha \) and \( \beta \) phases, ten phase diagram classifications have been proposed, including phase diagrams with peritectic and peritectoid transformations [29]. However, \( \beta \) stabilised titanium alloys tend to fall into the classifications of either simple transformation (\( \beta \)-isomorphous) or eutectoid transformation (\( \beta \)-eutectoid) as shown in Figure 2.2.

The focus of this work is primarily on the \( \omega \) phase, which is the key metastable phase in \( \beta \) titanium alloys. Whilst it can be argued that \( \beta \)-isomorphous and \( \beta \)-eutectoid additions result in different phase diagrams, the metastable phases that form are similar, making either system a viable study for \( \omega \) formation [30]. However, \( \beta \)-isomorphous systems are possibly easier to interpret from a fundamental viewpoint due to a smaller number of variables [22].

2.3 Phases in \( \beta \) titanium alloys

2.3.1 Parent and product phases

Parent phases can be described as regions of homogeneous material within which other physically distinct product phases can form. A parent phase can encompass the entire component or be divided into smaller regions known as grains. An example of a distinct product phase is \( \alpha \) precipitation that forms at \( \beta \) grain boundaries and as colonies of laths from the boundary into the grain [14, 31–34]. Whilst understanding the influence of the size and orientation of grains on material properties is important in engineering applications [25, 35, 36], this work focuses on phase transformations that occur within grains. For example, in the presence of multiple nucleation sites within the grain, several variants of the \( \alpha \) compete, leading to refined \( \alpha \) plates that have a chevron appearance [37]. As the density of nucleation sites
Fig. 2.2 Typical binary phase diagrams for $\beta$-isomorphous and $\beta$-eutectoid solute additions. Image reproduced from [29].
increases, the $\alpha$ precipitates become smaller and are described as super-refined [38, 39]. In $\beta$ titanium alloys specifically, $\alpha$ precipitation can be controlled and refined using the $\omega$ phase by providing intra-granular heterogenous nucleation sites. A two step age, first involving precipitation of the $\omega$ phase, followed by the $\alpha$ phase is a recently proposed tool for $\alpha$ phase refinement and results in a vast strength improvement [27, 40, 41]. It is still unclear, whether the $\alpha$ nucleates 1) within the $\omega$ precipitates [42–44], 2) heterogeneously on the $\omega/\beta$ interface [40, 45–47], 3) near but not on the $\omega/\beta$ interface [48], or 4) in regions without any $\omega$ present. In the latter case, $\alpha$ is thought to have precipitated in strained regions as a result of a $\beta$ phase spinodal decomposition [49]. Of particular interest is the nature of the resulting product phases and how they have transformed from the parent phase.

In $\beta$ titanium alloys, the parent phase is the $\beta$ phase which has a BCC arrangement of atoms; the $\beta$ phase unit cell is cubic with atoms at 0,0,0 and 1/2,1/2,1/2. The crystal structure could equally be described by the Im-3m space group with atoms at 0,0,0. The product phases, such as secondary phase precipitates can be described by a different unit cell. The product phases of particular interest to this project are the $\alpha$ and $\omega$ phases. The $\alpha$ phase has a hexagonal close packed (HCP) arrangement that can be described by the P63/mmc space group with atoms at 1/3,2/3,1/4. Whilst the lattice constants in the $\beta$ phase are equal in all directions this is not the case for the $\alpha$ phase. In the $\alpha$ phase the ratio between the c axis and the a axis ($c/a$) is approximately 1.6. The $\omega$ phase is also hexagonal but has the inverse $c/a$ ratio to the $\alpha$ phase. Using the same space group notation, the $\omega$ phase can be described by P6/mmm and atoms at 0,0,0 and 1/3,2/3,1/2. The atoms in the $\omega$ phase are not as closely packed as they are in the $\alpha$ phase, an indication that this arrangement is not as stable. However, the $\omega$ phase will be shown later to be closely related to the close packed $\beta$ phase and precipitate in preference to the $\alpha$ phase at temperatures less than 400°C [50].

### 2.3.2 Equilibrium and non-equilibrium phases

The properties of $\beta$ alloys are greatly improved by the co-occurrence of phases such as the $\alpha$ and $\omega$ phases. For example, $\omega$ precipitation increased the hardness of the commercial $\beta$ Ti-5Al-5Mo-5V-3Cr alloy by 15% when compared to the quenched condition [12]. In addition, a two step age ($\omega$ followed by $\alpha$) in Ti-12 wt.%Mo resulted in a strength of 1600 MPa [27]. Therefore, it is important to understand the conditions that promote multiple phases. Thermodynamic phase transformations can be explained by changes in the system free energy. Under a constant set of conditions, a secondary phase will form if the total free energy of the system is reduced by its formation. A stable equilibrium is reached when the
free energy of the system is minimised. Typically for titanium alloys, the two phases that minimise the system free energy by their formation are the $\beta$ and $\alpha$ phases. The $\beta$ and $\alpha$ phases are hence referred to as equilibrium phases. At different temperatures, different proportions and compositions of the two phases are required to minimise the total free energy of the system. Therefore, for any temperature change, the system must be given enough time to allow for diffusion of atoms to reach the new equilibrium and for phase transformation to finish.

Non-equilibrium product phases can form when $\beta$ alloys are cooled faster than diffusion can occur. These non-equilibrium phases are also referred to as metastable phases as a local free energy minimum is reached. The product phases typically form upon rapid cooling, such as water quenching, and proceed by a displacive transformation. A well established example of this transformation is the martensite transformation resulting in the formation of a martensite phase through cooperative displacement of atoms forming the new crystal structure. Two martensite phases are known to occur in titanium alloys, an $\alpha$ prime phase ($\alpha'$) and an $\alpha$ double prime phase ($\alpha''$) [51]. Both of these phases are transformation products from the parent $\beta$ phase. The $\alpha'$ phase has the same hexagonal crystal structure (HCP) as the $\alpha$ phase but differs in that it retains the $\beta$ composition. The $\alpha''$ phase has an orthorhombic structure which can be described by the Cmcm space group and atoms at 0,1/5,1/4. Martensite transformations can occur across many different classes of titanium alloys and are important considerations in $\beta$ titanium alloy design, especially for shape memory and super elastic properties [52]. However, a key characteristic of metastable $\beta$ alloys is the occurrence of another metastable phase, the $\omega$ phase, which can also form when the parent $\beta$ phase is rapidly cooled. The primary focus of this thesis will be the $\beta$ and $\omega$ phases, but considerations of the martensite and $\alpha$ phases are important in the data analyses.

The $\omega$ phase is found within metastable $\beta$ alloys following either quenching from the $\beta$ phase field or quenching and ageing below approximately 400°C. The $\omega$ phase formed following rapid cooling is termed athermal $\omega$ as the phase is compositionally indistinct from the $\beta$ phase (like the martensite phases). In contrast, isothermal $\omega$ is formed following heating to facilitate a long range compositional component (like the $\alpha$ phase). Therefore, the relative stability of the isothermal $\omega$ and $\alpha$ phases will vary with temperature whereas athermal $\omega$ is temperature independent. In general, the stable and metastable phase fields will vary between different systems [30] and with the amount of impurities such as oxygen present [53]. However, as a guide to the expected stability ranges, Figure 2.3 contains resistivity measurements during continuous heating of the metastable $\beta$ alloy Ti-15 wt.%Mo [54]. Since many microstructural changes will result in a change in resistivity, the derivative plot
2.3 Phases in β titanium alloys

Fig. 2.3 Continuous resisitivity measurements during heating of Ti-15 wt.%Mo. Regions I-V interpreted as: I) athermal ω dissolution, II) isothermal ω formation, III) isothermal ω dissolution, IV) α + β and V) β [54].

in Figure 2.3 can be used to determine phase stability ranges. The starting condition for this metastable β alloy was a solution heat treatment within the β phase field followed by a water quench. Region I is therefore attributed to the quenched β phase and the athermal ω phase. Following quenching, the material was heated slowly whilst the resistivity was measured. The changes in the resistivity shown in Figure 2.3 indicate the typical microstructural changes observed in metastable β alloys, although this technique is indirect and open to interpretation from supportive studies. For example, isothermal ω precipitation is irreversible and significantly effects the strength [12, 31, 55, 41], stiffness [56], resistivity [57–59] and thermal conductivity [57, 60–62] of the alloy. The following interpretation of Figure 2.3 is based on the aforementioned studies. Region I was attributed to athermal ω dissolution, region II as isothermal ω precipitation, region III as isothermal ω dissolution, region IV as equilibrium α formation and region V as equilibrium β [54]. The focus of this thesis is on the transformations associated with the athermal ω and isothermal ω phases within regions I and II, since these transformations will be critical for controlling α refinement and subsequent strengthening of metastable β titanium alloys.
2.3.3 Product phase transformations

Athermal and isothermal $\omega$ particles form homogeneously, are smaller than $\alpha$ precipitates and can be a large volume fraction within the parent $\beta$ grains. Therefore, both the athermal and isothermal $\omega$ precipitates could be used to control $\alpha$ precipitation. However, there are differences in the athermal and isothermal $\omega$ phases which may influence subsequent $\alpha$ nucleation. Athermal $\omega$ particles are highly directional, occur in the Å to nm size range and share the same composition as the parent $\beta$ phase. In contrast, isothermal $\omega$ precipitates have variable morphologies, are much larger and contain a distinct composition. The exact size of the isothermal $\omega$ precipitates is generally considered to be controlled by rejection of the solutes, and therefore, depends on the ageing time, temperature and species mobility [43, 63]. However, even during long duration ages, $\omega$ precipitates are sub 100 nm due to the homogeneous distribution restricting large scale growth [30].

The morphology of isothermal $\omega$ precipitates also depends on which $\beta$ stabilising elements are present in the $\beta$ alloy. It has been shown that the misfit between the product and parent phase is the determining factor for precipitate shape. The critical misfit between matrix and precipitate is quoted as 0.5%, below which precipitates are ellipsoid and above which the precipitates are cuboidal [30]. For example, in the low misfit Ti-Mo system, the precipitates were ellipsoidal with the major axis 3.5 times that of the minor axis [64]. In contrast, within the high misfit Ti-V binary, square cross section precipitates were observed [65].

In general, the equilibrium composition of isothermal $\omega$ is not well defined except that it is different to the composition of athermal $\omega$. Precise composition measurements in isothermal $\omega$ are not well established because the precipitates are still below the resolution of typical laboratory spectroscopy measurements [64]. Recently, advanced 3-dimensional composition mapping of isothermal $\omega$ precipitates using atom probe tomography has enabled quantitative partitioning measurements on a small length scale [2, 12, 38, 46, 66, 67]. However, in all of these cases, complex commercial alloys were used which means equilibrium isothermal $\omega$ compositions were difficult to establish. In the study of a simple Ti-Mo binary alloy, Ti-18 wt.%Mo, the isothermal $\omega$ precipitates were shown to have an average composition of 7.56 wt.%Mo after 30 minutes at 475°C [64]. However, it is questionable whether 30 minutes is enough time for diffusion at 475°C. On the other hand, some argue that lattice fluctuations away from the ideal $\omega$ structure (discussed later) can aid and enhance Mo segregation [68].
2.3 Phases in $\beta$ titanium alloys

Differences in size, morphology and composition between the athermal and isothermal $\omega$ phases are convincingly established. Therefore, in the transformation from athermal $\omega$ to isothermal $\omega$ it is reasonable to assume that the athermal $\omega$ either transforms to isothermal $\omega$ and coarsens, or isothermal $\omega$ forms heterogeneously on athermal $\omega$ [29]. In both cases, there is a structure change and a composition change. Consequently, it is discussed whether the composition component [69] or the structure component changes first [2, 29, 70]. In addition, there are other opinions of the athermal to isothermal $\omega$ transformation which further complicate this debate. For example, it has been proposed that the volume fraction of the athermal $\omega$ phase could increase by independent nucleation of more athermal $\omega$ prior to isothermal $\omega$ formation [67]. Interestingly, several indirect studies have suggested that athermal and isothermal $\omega$ are separate and proposed that athermal $\omega$ could dissolve (either partially or fully) before isothermal $\omega$ precipitates [54, 57, 61, 71]. These observations were based on reversible resistivity measurements at sub-diffusion temperatures and were subsequently rationalised by the presence of the athermal $\omega$ reducing the number of electrons in the conduction band [69]. However, unusual resistivity measurements (negative coefficient) were also suggested to be inherent to the $\beta$ phase rather than due to the athermal $\omega$ phase [72]. Therefore, more direct evidence of the transformation may be required to determine the athermal and isothermal $\omega$ transformation.

Recent advances in electron microscopy have enabled high magnification imaging of atom columns using a compositionally sensitive detector, making this technique ideal for investigating phases in metastable $\beta$ titanium alloys [2, 44, 73, 74]. Significantly, high resolution imaging has shown that the athermal to isothermal $\omega$ transformation may be more complex than previously thought and involve other non-equilibrium phases [7, 73, 75]. For example, new metastable phases were historically hypothesised by the observation of additional diffraction spots [76] but were shown by others to be double diffraction effects by tilt experiments [77]. With the advances in electron microscopy, complimentary diffraction pattern and high resolution direct imaging has shown that the spots previously attributed to double diffraction are a new phase. Figure 2.4 is a nano-domain of a non-equilibrium phase with an orthorhombic structure similar to but not the $\alpha''$ martensite phase [7, 75]. Interestingly, compositionally distinct orthorhombic structures have been reported during low temperature treatments in several $\beta$ alloys [73]. These could be attributed to the rich and lean products of the spinodal decomposition of the martensite phase previously reported [24, 78]. It is therefore possible that the spinodal decomposition of the non-equilibrium martensite phase may play a role in isothermal $\omega$ formation.
Fig. 2.4 A filtered HAADF along $<100>_{\beta}$ containing a recently reported nano-scale orthorhombic phase in Ti-Mo. Taken from [7].

In summary, direct observations of the athermal to isothermal $\omega$ transformation are difficult due to the presence of additional non-equilibrium phases in metastable $\beta$ titanium alloys. In fact, several studies have shown that observations of these metastable phases may not even be intrinsic to the bulk [79–84]. Critically, with respect to microstructure refinement, there are obvious benefits in fully understanding the athermal to isothermal $\omega$ transformation and subsequently the series of transformations plotted in Figure 2.3. However, due to the many possible metastable phases that could be involved in the production of a metastable $\beta$ titanium alloy, it is proposed that the most important step is the first. This often assumed step is a $\beta$ quench from the $\beta$ phase field and the formation of the athermal $\omega$ phase. This is the subject of the following section.
2.4 The athermal \( \omega \) phase in \( \beta \) titanium alloys

When metastable \( \beta \) titanium alloys are cooled following a heat treatment in the single \( \beta \) phase field, a single phase microstructure is almost never reported. This is true for both slow and fast cooling. From Figure 2.1, a metastable \( \beta \) alloy contains a stable equilibrium between the \( \beta \) phase and the \( \alpha \) phase at room temperature which means slow cooling will result in \( \alpha \) precipitation. However, this equilibrium is not reached when material cooling is rapid. Quenching is the process of rapid cooling and is normally achieved by the immersion of hot material into water. The aim of quenching is to retain the microstructure present at the point of quenching, which in this case, is the \( \beta \) phase. However, quenching from the \( \beta \) phase field normally results in a microstructure containing multiple phases; typically both the \( \beta \) phase and a compositionally indistinct \( \omega \) phase are present [22]. This is even the case when applying ultra rapid cooling rates [30]. The \( \omega \) phase observed following a rapid cool from the parent \( \beta \) phase field is termed the athermal \( \omega \) phase.

The athermal \( \omega \) particles are difficult to directly observe due to their size (20-40 Å) [29] and thus detection and interpretation of athermal \( \omega \) has relied on electron and X-ray diffraction based techniques [50, 65]. Despite the size of the particles and the difficulty in imaging, it is generally accepted that the athermal \( \omega \) precipitates are effectively linear-faults in the \( \beta \) phase aligned along the \(<111>_{\beta}\) directions [29]. Therefore, there are four variants of the athermal \( \omega \) phase, one for each of the four directions. Advances in microscopy have closely correlated with an improved understanding of \( \beta \) phase decomposition in metastable alloys [85]. Recently, there has been renewed interest in the formation of the athermal \( \omega \) phase due to the improved capability and accessibility of high resolution aberration corrected microscopes which enable direct observations of the \( \omega \) phase [5]. Data generated from these new technologies have resulted in the original theories of phase stability and transformation pathways being re-examined [6]. In the following sections, the evidence upon which those original \( \omega \) theories were built is discussed first. Then, the influence of high resolution microscopy on the current understanding of the athermal \( \omega \) phase is reviewed.

2.4.1 Understanding the athermal \( \omega \) phase using electron diffraction

The most established method to determine whether the athermal \( \omega \) phase is present in quenched microstructures is by using a transmission electron microscope (TEM). A conventional TEM (CTEM) operates by the illumination of a region of interest with relativistic electrons. These imaging electrons are typically generated from an electron gun vertically
above the sample and condensed into a beam by apertures and magnetic lenses. In contact with the sample, the imaging electrons can be scattered by the sample at the region of interest due to the crystal structure of the material. The majority of scattering is elastic scattering in the forward direction where the electrons conserve their energy. However, a small number of electrons will lose some energy to the crystal, causing them to scatter inelastically. An objective lens located beneath the sample in the forward direction re-focuses the scattered electrons to form an image on a detector. Due to the limited size of the objective lens, only coherent elastic electrons and incoherent inelastic electrons are used to form the image. Incoherent elastic interactions between the incident electrons and crystal, which normally scatter to a high angle, are lost [86, 87]. The importance of these lost electrons to understanding the athermal $\omega$ phase became clear while interpreting the phases observed in Chapter 4 and this is discussed in more detail there.

Generally, images of the athermal $\omega$ phase cannot be resolved in a CTEM due to the size of the particles. Typically, the only spatially resolved feature that can be seen is a mottled contrast within the parent material [65]. However, significant information can be attained by imaging the back focal plane of the objective lens. Within this plane, diffraction patterns can be viewed which show the elastic scattering from crystallographic planes as points of intensity in reciprocal space. In addition to this reciprocal space crystal information, the inelastic incoherent electrons scattering manifests as diffuse intensity between the Bragg diffraction reflections. Critically, both the parent $\beta$ phase and the athermal $\omega$ phase can contribute to diffraction pattern intensity in a TEM for certain orientations of the sample. Typically, either the $\langle 113 \rangle_\beta$ or $\langle 110 \rangle_\beta$ zones are utilised due to the presence of independent $\omega$ reflections. A schematic representation of these two indexed zones can be seen in Figure 2.5 [88]. Primary $\beta$ reflections can be observed where $h+k+l=2n$. However, these spots also contain information from the $\omega$ phase which cannot be distinguished. Independent $\omega$ reflections can only be observed at 1/3 and 2/3 $\langle 112 \rangle_\beta$. It should be noted that four different variants of the $\omega$ phase can occur. Figure 2.5 highlights that only two variants can be distinguished down any given $\langle 110 \rangle_\beta$ or $\langle 113 \rangle_\beta$ zones. The remaining two variants are contained within the $\beta$ reflections. Whilst the $\omega$ reflections are demarked by circles in Figure 2.5, the shape and intensity of the reflections differs in reality depending on a number of factors [89]. These observations become important when establishing the nature of the compositionally indistinct athermal $\omega$ phase found in material which was rapidly cooled from the $\beta$ phase field.
2.4 The athermal $\omega$ phase in $\beta$ titanium alloys

Fig. 2.5 An example of a diffraction pattern showing an array of diffraction spots resulting from constructive interference caused by multiple planes with the same structure. a) $<110>_{\beta}$ zone and b) $<113>_{\beta}$ zone diffraction patterns containing the $\beta$ and $\omega$ phases. All four of the $\omega$ variants cannot be viewed along any one $<110>_{\beta}$ or $<113>_{\beta}$. For each case, two distinguishable $\omega$ variants are identified. Reproduced from [88].

Many of the early theories about athermal $\omega$ were based upon diffraction pattern evidence. Variables such as species, concentration, temperature and imaging orientation were explored and conclusions determined about the athermal $\omega$ phase from the change in the diffraction pattern appearance. Figure 2.6 is a selection of diffraction patterns that give an overview of how such variables affect the diffraction spots associated with the athermal $\omega$ phase. In all cases, the diffraction patterns were taken from material which had been quenched from the $\beta$ phase field. Two binary systems were studied, Ti-Nb [18] and Ti-Mo [89].

The Ti-Nb was examined along the $<110>_{\beta}$ direction and the Ti-Mo along the $<113>_{\beta}$. In addition, the concentration of the Nb was changed in the Ti-Nb case and the TEM in situ observation temperature was changed in the Ti-Mo case. All of the diffraction patterns in Figure 2.6 contained intensity at 1/3 and 2/3 $<112>_{\beta}$, indicating that all of these images were of a $\beta$ matrix containing at least two of the four athermal $\omega$ phase variants. Temperature and alloy concentration were shown to affect the appearance of the $\omega$ intensities more than the different species and observation zone. Interestingly, decreasing the concentration had a similar effect on the diffraction pattern observed as decreasing the temperature. At low temperatures and compositions, the $\omega$ reflections at 1/3 and 2/3 $<112>_{\beta}$ are more intense than at room temperature and higher compositions. At higher compositions and temperatures, the maxima become weaker and are replaced by weak lines of uniform intensity extending between the primary $\beta$ reflections. These broad lines of intensity are occasionally referred to
Fig. 2.6 Diffraction patterns showing the variation in $\omega$ reflections with temperature and composition in $\beta$ titanium alloys Ti-Nb and Ti-Mo. From top to bottom in both cases: incommensurate $\omega$, diffuse $\omega$, athermal $\omega$ reflections and diffuse streaking and athermal $\omega$ with sharp reflections [29].

as diffuse $\omega$ reflections [90]. Lastly, at compositions approaching the stable $\beta$ phase field, the athermal reflections can become incommensurate, since the $\omega$ intensity is not precisely located at 1/3 and 2/3 $\langle 112 \rangle_\beta$ positions, a feature which also occurs in high misfit systems such as Ti-Cr [91] or at high solute concentrations [41, 85]. It is apparent from Figure 2.6 that any description of the athermal $\omega$ phase must be able to explain all of these observations.

A static description of the athermal $\omega$ phase can be used to rationalise the differences in the observed diffraction patterns with composition. This description is one of the two original models of the athermal $\omega$ phase. In the static description, the athermal $\omega$ particles form planes that have a unique spacing when compared to the $\beta$ phase. The volume fraction, size and distribution of the particles are used to rationalise the changes in intensity at 1/3 and 2/3
2.4 The athermal $\omega$ phase in $\beta$ titanium alloys

Specifically, the more atoms that form the $\omega$ structure, the more intense the $1/3 <112>_\beta$ and $2/3 <112>_\beta$ reflections become. The lowering of spot intensity at higher concentrations is therefore consistent with the formation of less $\omega$. The spot elongation or diffuse streaking associated with the $\omega$ reflections could be an indication of highly directional alignment or stacking disorder in the $\omega$ plane spacing. The streaks occur over 10-90% of the $1/3 <112>_\beta$ and $2/3 <112>_\beta$, corresponding to a disorder distance which is smaller than the $\omega$ unit cell. As previously stated, the ideal $\omega$ structure, where all atoms are located on a perfect crystal, has the symmetry group $P6/mmm$ and atoms at $0,0,0$ and $1/3,2/3,1/2$. However, for high concentrations of $\beta$ stabilisers, crystal structures that are not always the ideal, have been reported [22]. It is thought that a trigonal structure, or partial $\omega$ structure, can form with the space group $P-3m1$ and atoms at $0,0,0$, $1/3,2/3,1/2-Z$ and $2/3,1/3,1/2+Z$. When $Z=0$ the structure is the same as the ideal $\omega$ structure. Where $Z$ is greater than zero but less than 1/6 the trigonal structure can be regarded as a small perturbation from the ideal $\omega$ structure, which could account for the streaking. Under this static model, at higher concentrations it appears that not only is there less $\omega$ formation, the $\omega$ phase which has formed is more likely to have some trigonal nature [29].

Alternatively to the static model, a dynamical model of $\omega$ formation can also explain aspects of the streaking associated with the athermal $\omega$ phase in $<110>_\beta$ and $<113>_\beta$ zones [29]. In particular, the dynamic model better describes the changes in spot streaking with temperature. The dynamical model is based upon the close correspondence between the $\omega$ structure and the $\beta$ structure. The same $P-3m1$ trigonal description of the $\omega$ structure is used as in the static model: when $Z=0$ the atoms are arranged in the ideal hexagonal $\omega$ structure, when $Z=1/6$ the structure is identical to a perfect $\beta$ arrangement of atoms, and when $Z$ is between these values ($0<Z<1/6$) the structure is trigonal. This correspondence is shown in Figure 2.7, which is a 3-dimensional schematic illustration of a $\beta$ BCC unit cell with the vertical aligned to the $<111>_\beta$. Atoms in neighbouring cells are included to indicate how the two atom perfect BCC cell can be described using a three atom hexagonal ideal $\omega$ unit cell with the relation $\{111\}_\beta//\{0001\}_\omega$.

A key difference between the two models is that in the static model, the entire $\omega$ phase has the same value of $Z$ whereas the dynamic model allows each $\omega$ unit cell to have a different value of $Z$ on the continuum between perfect $\omega$ and perfect $\beta$ crystals. It can be seen in Figure 2.7 that to move from the perfect $\beta$ structure to the ideal $\omega$ structure, the atoms within the hexagonal unit cell must displace in opposing $<111>_\beta$ directions until they share a common plane. This can equally be described by the consecutive collapse
Fig. 2.7 Three-dimensional and two-dimensional relationship between the $\beta$ and $\omega$ phase. Diagram shows the collapsing \{111\}_\beta for commensurate and incommensurate $\omega$. Image taken from [92].

of two thirds of the \{111\}_\beta, as indicated by the lines in Figure 2.7. As a consequence, four $\omega$ variants can form depending on which of the four \{111\}_\beta are collapsing [30, 50]. Furthermore, for each \{111\}_\beta there are three sub-variants of athermal $\omega$ depending on which pair of planes collapse, giving a total of 12 possible sub-variants [92]. The dynamical model describes the parent $\beta$ phase containing a softening of the lattice with respect to a transverse $1/3<112>$ vibration mode or equivalent longitudinal $2/3<111>$ mode, Equation 2.2 [93].

$$U_e = \frac{a_\beta}{6} \sin[q_w x_1 + \phi(x_1)]$$

(2.2)

Where $U_e$ is the displacement, $a_\beta$ is the $\beta$ lattice parameter, $x_1$ is the plane position along [111]_\beta, $q_w = 2/3 < 111 >$ $2\pi/a_\beta$ and $\phi(x_1) = 0, 2\pi/3, 4\pi/3$ which represent the different variants [22, 93]. This phonon describes a vibrational mode in the $\beta$ phase in which two thirds of the \{111\}_\beta are vibrating with an amplitude that spans between the perfect $\beta$ structure and the ideal $\omega$ structure.

In support of the dynamic model, it has been reported that most BCC structures can contain softening of the $2/3 <111>_\beta$ wave vector due to unscreened coulombic interactions [94]. Additionally, pronounced softening in $\beta$ titanium towards a hexagonal structure is theoretically reasonable due to the fundamental preference for titanium atoms to assume
2.4 The athermal $\omega$ phase in $\beta$ titanium alloys

A hexagonal structure at lower temperatures. Subsequent electron-phonon coupling may form charge density waves (CDW) [94] causing athermal $\omega$ formation as a result of a charge density distortion of the $\beta$ phase [22]. The change in electron density associated with lattice distortions towards the $\omega$ structure may reduce the Fermi or free energy making this structure more energetically favourable.

The local free energy minima associated with phonon amplitude towards the $\omega$ structure is shown in Figure 2.8. This graph was constructed using a phenomenological model for the free energy that used a Landau expansion of free energy [95]. Within the expansion, the order parameter is the atomic displacements, or phonon amplitude, A, towards the $\omega$ structure [89]. The dynamical component oscillates around zero amplitude, with some oscillations large enough to overcome the $\beta$-$\omega$ energy barrier and reach the $\omega$ minima. These planes can become energetically pinned in the static description of $\omega$ minima for a lifetime determined by the barrier activation energy [95], resulting in intensity maxima at 1/3 and 2/3 $<112>_{\beta}$ within diffraction patterns. On rapid cooling, the position of the atoms in the $\beta$, $\omega$ or intermediate positions are frozen in place, resulting in diffuse streaking. Unlike the static description, the dynamic model can satisfactorily explain the variation in curvilinear streaking and incommensurate $\omega$ diffraction appearance with both temperature and concentration as resulting from coupling between the soft phonon and local vibrational modes away from the $<112>_{\beta}$ [29]. As the temperature decreases, the phonons will be less excited, which means more planes become pinned in the local minima, leading to sharper $\omega$ reflections at colder temperatures.

Currently, either the static model or dynamic model of athermal $\omega$ could explain the majority of the athermal $\omega$ diffraction phenomena that have been recorded. However, without direct observation of the athermal $\omega$ phase, the nature of this phase and the relevance of each theory are difficult to establish. For both models the maximum expected displacement of an atom (or largest Z) from the $\beta$ to $\omega$ structure is 1/6$a_{\beta}$. Typically, the lattice parameter of the metastable $\beta$ phase with alloy additions at room temperature is 3.276 Å and expands to 3.305 Å at 900°C. Transition metal additions such as Cr, Fe, Mo and Mn have all shown to decrease the lattice parameter [15]. Therefore, the maximum $\{111\}_\beta$ collapse distance is approximately 0.55 Å, a distance well below the resolution of most CTEM microscopes and preventing direct observation using current CTEM technology. However, modern high resolution techniques can resolve sub-Å features and are therefore useful tools for studying the athermal $\omega$ phase further.
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Fig. 2.8 Free energy, $A$, associated with the soft $\beta$ phonon towards the $\omega$ structure as calculated from phenomenal constants in the Landau equation. The dotted line shows harmonic approximation. Taken from [89].

2.4.2 High resolution imaging of the athermal $\omega$ phase

Coherent scattering is useful for understanding crystal structures because constructive and destructive interference of electrons are directly attributable to the crystal lattice. Coherent lattice imaging of the $\omega$ phase can be observed in the imaging plane provided the quality of the lenses is sufficient to achieve sub-nanometre resolution. This is known as high resolution (HR) imaging and can be achieved in several different ways. For example, one method is to use both round and non-round lenses to create opposing positive and negative spherical aberrations which then cancel out when used together [96]. However, despite significant reductions in the objective aberrations that would otherwise be present, it was found that lattice image intensity was sensitive to several coherent interference effects which made interpretation difficult. One such effect, image contrast reversal, is highly dependent on the defocus distance due to the additional path length of electrons changing the phase shift. However, this can be minimised by imaging at the Scherzer defocus [96]. Critically, phase contrast can also add features to an image which make interpretation indirect and much more complex. For instance, multiple scattering can result in contrast reversals and superposition of several crystal structures can form Moire fringes [97].
2.4 The athermal $\omega$ phase in $\beta$ titanium alloys

Using these techniques, high resolution TEM (HR-TEM) images of the athermal $\omega$ phase were shown to have weak modulated fringes that were additionally distorted by the two $\omega$ variants not contained within the observed [110]$_{\beta}$ zone [98, 99] and by dynamical scattering [100]. By using Scherzer defocus, phase differences were suppressed and images were of atom positions rather than lattice fringes [101]. However, even at the Scherzer defocus, lines of intensity in HR-TEM images were still identified around $\omega$ containing regions which meant further coherent image contrast simulations were required to confirm the presence of the phase [101].

Scanning transmission electron microscopes (STEM) are capable of eliminating the phase contrast effects observed in a conventional TEM. The difference between a STEM and a TEM is the position of the objective lens [87]. In a TEM, parallel electrons are incident on a sample and the scattered electrons are focused by the objective lens to form an image. In a STEM, the objective lens is above the sample and is used to focus the incident electrons so that they converge to a point on the sample. The convergent beam is then scanned across the area of interest similar to a scanning electron microscope (SEM). At each point in the scan, the probe dwells for a period of time. During this time, incident electrons are scattered by the sample and are not refocused to form an image. Instead, an annular detector is used to detect the scattered intensity within an angular range. During the dwell period the total intensity is incoherently summed over the entire detector and used to give an intensity value for one point on the sample. This procedure is repeated for each point in a scan to build up an image of the sample. By changing the effective distance between the sample and annular detector, the inner collection angle can be adjusted. This, therefore, changes the smallest angle that incident electrons need to scatter in order to reach the detector. In this setup, the annular detector is known as a dark field detector because regions where no scattered electrons have been detected appear dark in the final image [102].

HR-STEM imaging has distinct advantages over HR-TEM imaging since the annular dark field (ADF) STEM setup can detect the elastic incoherent interactions which are otherwise lost in the HR-TEM system. These elastic incoherent electrons can be detected in the ADF-STEM by positioning the ADF detector close to the sample. Therefore, only those electrons which have been scattered by high angles will be incident on the ADF detector. This setup is also known as high angle annular dark field (HAADF) imaging. Imaging using these electrons has three clear advantages. The first is the elimination of phase contrast effects [103]. This is because the electrons are incoherent and, therefore, do not interact with each other. Critically, this leads to direct image interpretation. The second advantage is
that high angle scattered electrons tend to scatter close to the nuclei. Therefore, incoherent interactions are more localised to the true atom position, which means spatial resolution is intrinsically better [102]. The third advantage is also linked to interactions with the nucleus. The scattering is analogous to Rutherford scattering, which means the atomic number of the nuclei can affect the degree of scattering [86]. This means HAADF imaging contains sensitivity to local atomic number and can be used to determine local composition.

In modern aberration-corrected HR-STEM microscopes software is used to optimise aberrations in the objective lens [104]. The combined technology of aberration corrected lenses with HAADF detectors allowed the $\beta$ and athermal $\omega$ phases to be directly observed [5, 6]. Figure 2.9a is a HAADF image of rapidly cooled material viewed down $<110>_{\beta}$. Atoms in the $\beta$ and $\omega$ structures are indicated by the white rectangular boxes and show the hexagonal unit cell when viewed along this direction. The collapse of 2/3 of the $\{111\}_{\beta}$ can be seen in the $\omega$ unit cell. Critically, a partial collapse of the $\{111\}_{\beta}$ was resolved. Figures 2.9b-d illustrate this collapse of the $\{111\}_{\beta}$ from the perfect $\beta$ structure (Figure 2.9b) to the ideal $\omega$ structure (Figure 2.9d). Using the notation from Figure 2.9, planes B and C collapse in opposing directions to form plane B’. A partial collapse is when the planes lie between B and C but not at B’. The $\omega$ cell in Figure 2.9a appeared more like Figure 2.9c than Figure 2.9d. Therefore, the athermal $\omega$ was thought to have a trigonal structure, an observation supported at other concentrations [7].

HR aberration corrected STEM imaging of atoms with a HAADF detector can be used to probe alloy structure on an appropriate length scale to observe $\{111\}_{\beta}$ collapse, making it ideal for understanding the athermal $\omega$ phase. However, although HAADF imaging is a two-dimensional technique that appears to record arrays of two dimensional Gaussians representing atoms, in fact the HAADF images are actually of atom columns and not individual atoms. This is because the imaging electrons have passed through the thickness of the sample before being detected, which means HAADF images are two-dimensional projections of the three-dimensional structure. Therefore, whilst HAADF images are directly interpretable, thickness effects can alter the apparent position and intensities of the atoms. For example, the extent of apparent collapse is thought to change depending on the volume fraction and proximity of the $\omega$ phase to the exit surface [105]. The following section looks at how HAADF images can be used to understand the three-dimensional structure.
Fig. 2.9 a) A filtered high resolution HAADF image along $<110>\beta$ containing the $\beta$ and $\omega$ structures which are indicated in the white boxes. This image shows the partial collapse of $\{111\}_\beta$ planes. b-d) Illustration of the progressive collapsing of the $\{111\}_\beta$ from the perfect $\beta$ structure (b), through partial collapse (c) to the ideal $\omega$ structure (d).
2.4.3 Interpreting incoherent images of the $\omega$ phase

The athermal $\omega$ observed in HAADF images was identified by the consecutive collapse of 2/3 of the $\{111\}_\beta$. There are several conflicting interpretations of the apparent position of the shifted atom columns in relation to the three-dimensional structure [5, 105]. On one hand, it is argued that atoms in the $\omega$ phase are not fully collapsed, which would mean the local structure is trigonal [5]. Alternatively, it has been suggested that beam channelling between the parent and product phases along the beam direction can result in the appearance of partial collapse [105].

Computer calculations are useful tools to aid the interpretation of HAADF images and investigate the associated three-dimensional structure. Several computational approaches have been taken including theoretical modelling, simulations and bulk data processing. The first approached used was *ab initio* energy calculations of the $\omega$ phase comparing partial and complete collapse of the $\{111\}_\beta$. This used a density functional theory (DFT) approach which effectively solved a many electron Schrödinger’s equation, Equation 2.3.

$$E\Psi = \hat{H}\Psi$$

Where $E$ is the total energy and $\hat{H}$ is the Hamiltonian applied to the bound electrons wave function, $\Psi$. By only considering electron density, $\rho$, DFT calculations substitute the Hamiltonian, $\hat{H}$, for a series of functionals, Equation 2.4, to solve for the system enthalpy at 0°C.

$$E(\rho) = T(\rho) + E_{en}(\rho) + E_{ec}(\rho)$$

Whilst the energetic contributions of kinetic energy, $T$, and the electron-nuclear interactions, $E_{en}$, are directly solvable, the contributions of the electron-electron interactions are not. Therefore, the exchange-correlation function, $E_{ec}$, is substituted and an iterative computational method is applied to find the lowest energy solution. The two most frequently used exchange-correlation functionals are the local density approximation (LDA) and the local generalised gradient approximations (GGA). However, it has not yet been established which is the correct choice when applied to $\omega$ phase. Some calculations performed indicated that there is a local energy minima associated with partial collapse and the extent of this collapse corresponds to the measured collapse in the HAADF images [6]. However, the level of information that can be gained from the comparison of these 0°C calculations to a structure
It can be argued that simulated HAADF-STEM images have been derived from more realistic calculations which included known microscope parameters, thereby making them more reliable. Different three-dimensional structures have been simulated and compared to actual HAADF results [105]. This method of simulation uses a multi-slice approach where the sample is split up into slices separated by vacuum. An atomic potential is then calculated for each slice, with the effects of electronic rearrangement from bonding ignored. For one position in the simulated HAADF image, \( r_p \), a probe wave function, \( \psi_p(r, r_p) \), is generated following the convolution of a wave function with simulated objective aberrations. A transmitted wave function is then created by the convolution of the probe function with a transfer function, \( t(r) \), as shown in Equation 2.5.

\[
\psi_t(r, r_p) = \psi_p(r, r_p) \otimes t(r)
\]  

(2.5)

The transmission function is composed of imaginary and real parts to simulate the coherent (phase) and incoherent (amplitude) interactions between the probe and the calculated atom potential. The transmitted wave function is then propagated across a hypothetical vacuum between slices before subsequent interaction with all of the other slices in the same way. After transmission and propagation through each of the slices, the diffracted wave, \( \Psi_t(k, r_p) \), is evaluated by the Fourier transform (FT) of the final transmitted wave function. This is shown in Equation 2.6.

\[
\Psi_t(k, r_p) = FT[\psi_t(r, r_p)]
\]  

(2.6)

The annular detector intensity is simulated by incoherently summing the diffracted wave amplitude over an angular range using Equation 2.7.

\[
g(r_p) = \int D(k)|\Psi_t(k, r_p)|^2d^2k
\]  

(2.7)

Where \( D(k) = 1 \) on the detector otherwise 0 and \( g(r_p) \) is the vector position to an x,y pixel coordinate and in the HAADF simulation. This whole process is then repeated for each pixel to form the final HAADF simulated image.
Using multi-slice simulations, it has been shown that the position and volume fraction of the ω phase can change the apparent position of the \{111\}_β when using HAADF imaging [105]. The volume fraction effect is intuitive. Within each atom column there may be a mixture of atoms within the β and ω phases. When the beam passes through a higher proportion of atoms in the ω structure relative to the β structure, the resulting position of the entire atom column appears shifted more towards the ω structure. However, these multi-slice simulations also indicated that the positional effect was greater than that of the volume fraction. For example, when the simulated ω was trigonal and the atoms only shifted by 25% of the ideal structure, the apparent shift was largest for the smallest volume that was closest to the surface. Interestingly, this was only the case for when the ω was located at the top surface where the beam entered the material rather than at the exit side. This suggests that the probe defocus is important when considering the extent of collapse since a 0 nm defocus on an ω structure at the top surface showed ideal ω, whereas the same defocus when the ω is located at the exit surface showed perfect β. This indicates that only very small thicknesses (15 nm) might actually be imaged in HAADF setups [105].

Image processing is the third computational method that can be used to interpret the ω phase. It is becoming standard practice to filter HAADF images to improve image clarity. However, the processing applied to images is not always reported. One commonly used filter is a band-pass filter which removes high and low frequencies within the image using a Fourier method. The Fourier transform of a HAADF image is analogous to Equation 2.6 and by shifting the low frequencies to the centre the frequency map will appear similar to a CTEM diffraction pattern. In addition to the lattice periodicities of interest, frequencies not attributable to the material can be present in HAADF images. For example, probe instability will result in high frequencies and detector flatness in low frequencies within the diffractogram. A bandpass filter can mask these high and low frequencies such that when the image is inverse Fourier transformed, they will be removed. The resulting filtered image is cleaner and smoother than the raw image, which can aid the interpretation of the lattice frequencies. However, care must be taken to not remove or alter features that are intrinsic to the material or add artefacts by constraining the processed image to only a sub-set of frequencies. Therefore, despite the fact that incoherent imaging can be directly interpretable, caution should be exercised when analysing and drawing conclusions from images that have been filtered.
2.4 The athermal \( \omega \) phase in \( \beta \) titanium alloys

2.4.4 Observations of site occupancy within the athermal \( \omega \) phase

In HAADF images of Ti-5Al-5Mo-5V-3Cr (wt.\%), local intensity variations have been observed within the athermal \( \omega \) phase, with the collapsing \{111\}_\beta planes exhibiting a lower intensity than the non-collapsing planes [106]. Specifically, in images down the \( <110> \)\_\beta, when plotting the intensity of atoms along a \( <200> \)\_\beta, the intensity follows a bright-dark-dark periodicity corresponding to a single stationary and two collapsed \{111\}_\beta planes, shown in Figure 2.10. This has been termed tri-layer periodicity [106] and has significant implications for the nature of the athermal \( \omega \) phase.

Incoherent scattering to a HAADF detector means the signal will contain significant amplitude contrast and negligible phase contrast. Therefore, Equation 2.7 can be approximated as Equation 2.8.

\[
g(r) = f(r) \otimes h_{ADF}(r)
\]

Where \( f(r) \) is the probability of scattering to the HAADF detector and \( h_{ADF}(r) \) is the square of the incident probe wave function modulus. Correspondingly, the incoherent scattering intensity, \( g(r) \), has been shown to be proportional to \( Z^\alpha \), where \( Z \) is the average atomic number down an atom column and \( \alpha \) is in the range 1.5-2 [102, 107]. Consequently, the tri-layer periodicity observed in \( \beta \) quenched material was attributed to variations in the local composition, which suggests preferential site occupation and possibly ordering within the \( \omega \) phase [105, 106].

Ordering of \( \beta \) stabilising elements in the \( \omega \) structure has been investigated prior to HAADF studies but lacked supporting evidence [108]. The bonding induced atomic ordering (BIAO) theory argued the two different sites (collapsing and non-collapsing) in the \( \omega \) structure have different preferences for different species due to a change in local environments [109]. This was based on an apparent independence of \( d_{111} \) with composition [110]. In agreement, \textit{ab initio} studies have shown an effect of electronic density on bond distances in the \( \omega \) phase [111–113], which means different species can exhibit a preferential site occupancy at 0K. Therefore, local structure within the \( \omega \) phase is feasible.

In addition to Ti-5Al-5Mo-5V-3Cr (wt.\%), intensity variations between the collapsing and non-collapsing planes have also been observed in rapidly cooled Ti-18 wt.\%Mo [5] and in Gum metal (Ti-31.9Nb-2.0Ta-2.7Zr-0.3O wt.\%) [105] when imaged under HAADF condit-
Fig. 2.10 High resolution raw and filtered HAADF images along \(<110>_\beta\) showing intensity modulations along \(<200>_\beta\) termed tri-layer periodicity. Taken from [106].
tions. In fact, the tri-layer periodicities were very similar despite the considerable differences in alloying elements. However, if all the atoms were homogeneously distributed, the corresponding average atomic numbers would be 21.8, 26.5 and 24.0 for Ti-5Al-5Mo-5V-3Cr, Ti-31.9Nb-2.0Ta-2.7Zr and Ti-18 wt.%Mo respectively. Therefore, if the heavier $\beta$ stabilising elements were re-locating to the non-collapsed planes, contrast would predominantly be the result of local variations of Nb ($Z=41$) and Mo ($Z=42$) which are only one atomic number apart from each other and approximately twice that of Ti, V and Cr ($Z=22-24$). Similarly, if the $\alpha$ stabilisers were residing on the collapsing $\{111\}_\beta$, an increased amount of Al would be responsible for a decrease in atom column intensity.

Significantly, it was shown that the tri-layer periodicity could be reproduced in HAADF simulations when the heavier additions are located solely on the stationary $\{111\}_\beta$ planes. However, the tri-layer periodicity was also shown to be reproducible in HAADF simulations entirely without the presence of element additions [105]. This composition independent observation could account for the large area over which the tri-layer periodicity has been recorded. Without further evidence, the origin of the tri-layer signal cannot be deduced.

### 2.5 Spinodal decomposition in $\beta$ titanium alloys

Precipitation of the isothermal $\omega$ and $\alpha$ phases is understood to be a first order transformation consisting of a classical nucleation and growth model. However, initial compositional redistribution prior to nucleation might suggest a $\beta$ decomposition with second order behaviour [30, 69, 114]. Spinodal decomposition can be difficult to identify but its presence might be important for describing phase transformations. Specifically, a new theory for the mechanism of athermal $\omega$ phase formation relies on the spinodal decomposition of the $\beta$ phase. If spinodal decomposition is a part of $\omega$ formation [6], then $\omega$ precipitation will be intrinsically different between systems that contain a miscibility gap and those that do not. In terms of strength improvements, a spinodal decomposition of the $\beta$ phase could refine the $\alpha$ phase without the need of two step processing as the strain between solute rich and lean regions could provide adequate nucleation sites for the $\alpha$ phase [115]. This section examines the non-classical decomposition of the $\beta$ phase followed by subsequent secondary phase formation.

The spinodal decomposition of the $\beta$ phase into solute rich and lean phases is a much debated topic in metastable $\beta$ alloys. Early phase diagrams did not include a monoeutectoid reaction
in many $\beta$-isomorphous systems [21, 116], possibly because early work relied on optical microscopy and limited laboratory X-ray diffraction techniques. The binary phase diagrams now include a miscibility gap in $\beta$ phase field for several $\beta$-isomorphous systems such as Ti-Mo, Ti-W and Ti-V but not in Ti-Nb. Convincing evidence of $\beta$ phase decomposition links microstructural observations, diffraction analysis and chemical alterations. However, consistent evidence that links multiple techniques together is sparse. Therefore, each observation is considered in turn.

Theoretically, spinodal decomposition occurs at temperatures where the free energy curve contains a double well [117]. Accordingly, this only happens when the system contains a positive enthalpy of mixing, $\Delta H_{\text{mix}}$. By drop calorimetry, the $\beta$ phase of pure titanium has been shown to contain a positive $\Delta H_{\text{mix}}$, making spinodal decomposition in $\beta$ titanium a distinct possibility [118]. Concerning $\beta$ binaries, the $\beta$-isomorphous Ti-Mo, Ti-Nb and Ti-V were all predicted to contain a miscibility gap [119] but of these, only Ti-Mo and Ti-V were shown to have a large positive $\Delta H_{\text{mix}}$ [120] for the monotectoid reaction to be possible. However, for a positive $\Delta H_{\text{mix}}$, atoms must have a preference for similar neighbours over unlike neighbours, which was not found for short range order calculations in Ti-Mo [121, 122].

Some reported evidence for a spinodal microstructure can be found in CTEM images. Diffracting features within a $\beta$ matrix of Ti-Cr ($\beta$-eutectoid) and Ti-Mo ($\beta$-isomorphous) were determined to be the result of a spinodal decomposition [123–125]. However, these features had a precipitate appearance and did not exhibit a characteristic wavelength. Additionally, diffraction spot analysis of these features gave no additional phase or compositional information. Whilst diffraction spot splitting is an indication of composition variations within the phase, CTEM first order reflections can often obscure small distortions in shape due to detector saturation. Higher order reflections mean subtle differences in the lattice parameters are enhanced. Therefore, until recently, the most convincing evidence for $\beta$ decomposition was the observation of X-ray peak splitting [126, 127]. However, as only single peaks were considered, the asymmetry of the reported high angle peak could be due to precipitation of either $\alpha$ or $\omega$ particles and not $\beta$ splitting.

Recently, HR-STEM microscopy was used to observe spinodal behaviour. The imaging of atom columns down low index zones provided real space structural information. When these images are Fourier transformed, frequency information analogous to the zone diffraction pattern can be seen. The frequency can be superior to a CTEM diffraction pattern as the
2.5 Spinodal decomposition in $\beta$ titanium alloys

information is from much more localised regions and does not include saturation effects [128, 129]. The Fourier transform of a high resolution image taken from a $\beta$ alloy shows some spot splitting consistent with a phase split. However, additional spots are also present in conjunction with the split spots, therefore, the conclusion drawn here is that splitting may not be due to a spinodal decomposition.

The most recent convincing evidence for a spinodal decomposition utilised a HR-STEM with a HAADF detector [5, 6, 130]. Under these conditions, image intensity is proportional to the square of the average atomic number down a column. Figure 2.11 is an atom column image of $\beta$ quenched (Ar cooled at 10 °C/s) Ti-18 wt.%Mo in which the brighter regions can be interpreted as a higher concentration of Mo. Although no clear wavelength is evident, a compositional fluctuation of approximately 4 nm is present [5, 6, 131]. In this description, the $\beta$ phase separates into solute rich and lean regions of titanium. The pockets of material with small quantities of $\beta$ stabilisers are then thought to be subsequently prone to a spontaneous displacive transformation to the $\omega$ structure on cooling. It is thought that at lower temperatures, the free energy curve for the $\omega$ phase intercepts that of the $\beta$ lean minima of the $\beta$ curve. This may possibly explain why maxima are sometimes observed during the quench once the isothermal phase field has been intercepted [30]. Critically, this transformation mechanism can only apply to systems with a reported spinodal behaviour and is therefore not general across both eutectoid and isomorphous systems.

The existence of a miscibility gap is important as it could play a role in secondary phase precipitation as the formation of solute rich and lean regions could lead to local destabilisation towards $\alpha$, martensite and $\omega$ [132]. In addition, control of the spinodal wavelength could be a key factor for influencing the size of secondary precipitates. For example, the composition wavelength will be dependent on temperature and, therefore, the $\beta$ solutionising temperature may become important. In agreement, $\alpha$ precipitates are shown to vary dramatically in size with $\beta$ quench temperature [133], which might be the influence on a $\beta$ phase decomposition.

Alongside the conventional view of $\alpha$ precipitation (nucleation and growth), $\alpha$ has also been observed to be the product phase of two compositional fluctuations, one involving compositional fluctuations in the $\beta$ phase [115] and the second from the decomposition of the martensite phase [24, 78]. Consequently, a pseudo-spinodal mechanism for $\alpha$ precipitation has been hypothesised [115]. Specifically, homogeneous $\alpha$ precipitation was observed during step quenching from the $\beta$ phase field to the $\alpha$$+$$\beta$ phase field to avoid the influence of the $\omega$ phase or a $\beta$ spinodal decomposition. The $\alpha$ precipitates appeared to have homogeneously
Fig. 2.11 Raw and filtered HAADF images taken along $<110>_{\beta}$ showing a variation in contrast which is attributed to $Z^2$. Taken from [5].
2.5 Spinodal decomposition in $\beta$ titanium alloys

Fig. 2.12 A bright field TEM image of a modulated spinodal appearance as a result of the decomposition of the martensite phase, $\alpha''$, to form $\alpha$. Taken from [78].

nucleated with the $\alpha$ structure and with compositions similar to small $\beta$ composition fluctuations [115]. This mechanism is thought to be entirely independent of $\omega$ precipitation yet results in super refined $\alpha$ that is similar to when $\omega$ directly or indirectly influences the $\alpha$ nucleation [38, 39, 134]. However, in the pseudo-spinodal mechanism, the $\alpha$ precipitates are on the same length scale as the compositional modulations, which are temperature dependent, therefore, this mechanism provides an additional way to refine the $\alpha$ phase [115].

Lastly, the $\alpha$ phase has also been shown to form via a spinodal decomposition of the orthorhombic martensite phase, $\alpha''$. This was observed in several $\beta$ alloys [24, 78] which were also thought to have a $\beta$ decomposition. However, unlike $\beta$ phase decomposition, this decomposition had clear periodicity, as shown in Figure 2.12. Whilst no more direct evidence of an orthorhombic decomposition has been reported, recently, compositionally distinct orthorhombic phases have been observed [58, 73, 129, 135, 136]. These orthorhombic phases could be related to the rich portion of the spinodal decomposition, with the lean phase transforming to the $\alpha$ phase.
2.6 Ti-Mo case study

The mechanical properties of $\beta$ titanium alloys, particularly increases in strength, are to a large extent dependent on the precipitation of the $\alpha$ and $\omega$ phases [137]. Some variability in strength will also depend on exact alloy composition, as each alloy will have a different resistance to dislocation motion in the $\beta$ matrix. This resistance is due to a variation in the generated strain field when elemental additions are substituted into the titanium lattice [19]. For example, in the Ti-Mo system, Mo atoms are smaller than the Ti atom resulting in compressive strain fields [121]. However, the variability in substitutional strengthening that is seen between different alloys is insignificant compared to the strength increases that can occur as a result of precipitation hardening across all alloys [137, 138]. Therefore, when developing strengthening mechanisms, representative simple $\omega$ forming binary systems should be used.

In this thesis, the Ti-15 wt.%Mo alloy was selected for investigation for several reasons. Primarily, titanium alloys with approximately 15 wt.% Mo $\beta$ stabilisation were historically the choice alloys upon which many of the theories were developed [6, 50, 89]. This makes Ti-15 wt.%Mo alloy a prototype binary alloy [29]. The advantage of studying an alloy in the isomorphous Ti-Mo system is that Mo has a larger scattering factor when compared to Ti [20]. This was particularly important in the studies of the athermal $\omega$ phase because much of the phase characterisation was deduced from CTEM and laboratory X-ray scattering experiments. With easier accessibility to high energy synchrotron facilities, high quality scattering data is being acquired for Ti-15 wt.%Mo [139]. By exploiting the difference in scattering factors in synchrotron scattering, it may only now be possible to establish any local structure in the metastable $\beta$ alloys, for example detecting the positions of the Mo atoms in the $\omega$ phase. Concurrently, Ti-Mo alloys are also useful materials to investigate using modern HAADF-STEM techniques. This is because the HAADF detector is sensitive to Z and the atomic numbers of Ti and Mo are 22 and 42 respectively. Therefore, a column of Mo atoms is expected to be approximately 4 times more intense than a column of Ti atoms. Therefore, when using the latest techniques, the Ti-15 wt.%Mo alloy is just as an applicable model alloy as it was 60 years ago.

Naturally, it follows that many commercial multi-component metastable $\beta$ alloys are based on approximately 15 wt.% equivalent level of $\beta$ stability, as shown in Figure 2.13. Therefore, any observations in Ti-15 wt.%Mo can be considered commercially useful for metastable $\beta$ alloy developments in Ti-5553, Timetal 21S, LCB or Beta-C products for high speed aircraft applications [14, 140]. Furthermore, performance of turboengine parts made from $\alpha/\beta$ titanium alloys such as Ti-6Al-4V (Ti-6-4) and Ti-6Al-2Sn-4Zr-2Mo (Ti-6242) rely on
a precise understanding of the microstructure [141]. However, little consideration has been made concerning the possible presence of the \( \omega \) phase within \( \alpha/\beta \) alloys and the effect this may have on mechanical properties. For example, athermal \( \omega \) may occur within any retained \( \beta \) phase that contains a Mo equivalence smaller than 25 wt.%. Therefore, Ti-15 wt.%Mo is applicable to multiple classes of titanium.

Lastly, the Ti-15 wt.%Mo alloy is of particular interest because this alloy has shown promising behaviours [142, 143], which could lead to applications beyond high strength products. Originally, Ti-15 wt.%Mo alloy was examined for its superconductive properties due to the \( \omega \) phase pinning flux [142]. However, this has not seen application since non-metallic systems typically perform better. The more useful behaviours are the martensitic transformations [143] which could lead to super-elastic or shape memory properties. Two applications related to these properties are orthopaedic implants [144] and intelligent engine airflow fins [145]. The implants would utilise the corrosion resistance and biocompatibility of Ti-Mo based alloys in conjunction with a tailored transformation such that the effective elastic modulus is closer to bone than Ti-6Al-4V [146]. In contrast, the intelligent jet engine air flow fins would combine reversible thermal transforms with high strength to guide airflow to minimise the mass, number of parts and primarily the noise of an engine. In both of these cases, the \( \omega \) phase influences the extent to which these behaviours occur. For example, the presence of the isothermal \( \omega \) phase is known to suppress martensite formation [40], however, microstructures which do contain the martensite appear to contain an elevated quantity of the athermal \( \omega \) phase [147]. In addition, the athermal \( \omega \) is seen to form in twin bands associated with the martensite transformations [88]. Critically, it is often shown that one variant of the \( \omega \) phase becomes dominant [148]. Subsequently, stress induced variant selection during deformation has been proposed [149–151], however, these reflections could be attributed to double diffraction [65], or simply that the \( \omega \) structure can also be described as a \( \beta \) twin boundary [152–154]. These complex \( \omega \)-martensite relationships will need to be explored and understood prior to application.
Fig. 2.13 Commercial alloys ranked according to their Mo equivalence (using equation 2.1).
2.7 Objectives and aims

There is still some uncertainty concerning phase stability in the Ti-Mo $\beta$-isomorphic system. Two of the possible Ti-Mo phase diagrams are overlaid in Figure 2.14 [116]. Initially, from optical microscopy and early X-ray diffraction data, it was concluded that Mo had complete solubility in the $\beta$ phase [21]. In contrast, observations of isolated high angle diffraction peaks provided evidence for a chemical spinodal and thus a monoeutectoid reaction [126, 156]. Critically, our understanding of the formation of the $\omega$ phase is dependent on which of these theories is correct. Therefore, further research is needed to expand the evidence base for this interesting area of contention. Quite noticeably within the literature, there was a lack of Ti-15 wt.%Mo characterisations which combined different complementary techniques following thermal treatments for long durations. In particular, no evidence of energy dispersive X-ray (EDX) spectroscopy of the $\omega$ has been reported, possibly as these precipitates cannot be resolved in an SEM. However, an EDX-STEM system may have the capability. Therefore, the first objective of this work was to characterise Ti-15 wt.%Mo following 500 hour heat treatments over a 300-800°C temperature range using SEM, X-ray, TEM and hardness techniques.
The second ambiguity in the literature is that between the static and dynamic theories of athermal $\omega$ formation, no one theory is deemed better. Therefore, the second objective of this thesis was to understand the nature of the athermal $\omega$ phase and, thus, distinguish between the two theories. On one hand, the dynamic theory transfers across isomorphous and eutectoid systems, however, it is only inferred from reciprocal space effects and phenomenological models. In contrast, the static description, which was originally also only based on reciprocal space effects, has now been directly observed in real space. Critically, it has been recently found that direct imaging of atom columns may not be simple to interpret [105] and should not be taken at face value. In addition, the chemical alterations were primarily concluded from filtered HAADF images rather than spectroscopy. Therefore, the second aim was to examine the possibility of local structure using high resolution imaging, modelling and electron energy loss spectroscopy (EELS) analysis.

The last objective of this thesis was to gain a better understanding of the athermal to isothermal $\omega$ phase transformation using *in situ* and *ex situ* techniques. In particular, an attempt was made to separate the displacive and composition components of the transformation in order to characterise the transformation pathway. Specifically, to see how athermal $\omega$ is related to the isothermal $\omega$ by examining any dissolution of the athermal phase before precipitation of the isothermal phase. Through understanding the transformation sequence, it may be possible to determine if the $\omega_{\text{ath}} \rightarrow \omega_{\text{sto}}$ transformation is mixed-mode similar to that of the recently proposed athermal $\beta \rightarrow \omega$ transformation. This understanding might aid with maximising $\alpha$ precipitation sites to strengthen metastable $\beta$ titanium alloys following a two step age.

In summary the objectives and aims of this work are:

- To characterise phase stability and elemental partitioning of Ti-15 wt.%Mo following long duration thermal exposures. The aim is to find evidence for a spinodal decomposition.

- To investigate the possibility of local structure and the nature of the athermal $\omega$ phase in material quenched from the $\beta$ phase field. The aim is to determine if Ti-15wt. %Mo follows the static or dynamic theory of athermal $\omega$ formation.

- To explore the athermal to isothermal $\omega$ phase transformation using *in situ* and *ex situ* techniques. The aim is to determine if the athermal $\omega$ dissolves prior to isothermal $\omega$ formation.
Chapter 3

Heat treating Ti-15 wt.% Mo

3.1 Introduction

Metastable $\beta$ titanium alloys are alloys that contain less than 25 wt.% Mo equivalence and do not have a fully stabilised $\beta$ phase [30]. Phase decomposition is so integral to these alloys that single phase microstructures are rarely reported or used commercially [23]. The decomposition products have engineering significance as they impede dislocation motion and thereby increase the strength. Different ageing temperatures can change the size, volume fraction, distribution and structure of the precipitates [137, 157], which is why metastable $\beta$ titanium alloys have an excellent age hardening response [58]. In particular, the Ti-15 wt.%Mo alloy has been the focus of many studies due to early commercialisation for its superconductivity properties [35, 142] and has subsequently become a model binary alloy in the Ti-Mo system to investigate metastable phase stability [5].

The $\beta$ matrix in titanium alloys is ductile as the structure can facilitate dislocation motion, typically with a $\frac{2}{3}<111>$ Burgers vector [158]. Every $\beta$ alloy will have a slightly different inherent resistance to dislocation motion in its matrix due to variation in the generated strain field when elemental additions are substituted into the $\beta$ lattice [19]. Therefore, some variability in strength will depend on exact alloy composition. In the Ti-Mo system, Mo atoms are smaller than Ti atoms resulting in compressive strain fields that inhibit dislocation glide [121]. However, the variability in substitutional strengthening that is seen between different alloys is insignificant compared to the strength increases that can occur as a result of precipitation in these systems [137, 138]. As a result of this, the mechanical properties of $\beta$ titanium alloys are, to a large extent, dependent on the precipitation of the $\alpha$ and $\omega$ phases.
As previously discussed in Chapter 2, the nature and formation of the $\alpha$ and $\omega$ phases in metastable $\beta$ alloys are still debated. Whilst structural information has been extensively studied, compositional information on a local length scale has not been characterised as well. Recent studies using atom probe tomography have had some success [2, 12, 38, 39, 46, 66], however, the origin of chemical signal in multi-component alloys can be difficult to distinguish [67, 105, 106]. A binary system with a large distinction between atomic numbers, such as titanium, Ti ($Z=22$) and molybdenum, Mo ($Z=42$), is more suitable for direct interpretation. However, even in model simple systems such as Ti-15 wt.%Mo, complexity is apparent.

Differences in interpretation of results obtained from Ti-15 wt.%Mo alloys arise due to uncertainty concerning phase stability in the Ti-Mo $\beta$-isomorphous system. Two of the possible Ti-Mo phase diagrams are overlaid in Figure 2.14. Initially, from light microscopy and early X-ray diffraction, it was concluded that Mo had complete solubility in the $\beta$ phase [21]. However, in contrast, observations of isolated high angle diffraction peaks provided evidence for a chemical spinodal and a mono-eutectoid reaction [116, 126, 156]. Critically, an understanding of the formation of the $\omega$ phase is dependent on which of these theories is correct. Recent research using Ti-18 wt.%Mo supports the second theory as evidence was found for spinodal decomposition of the $\beta$ phase [6]. This result was interesting as this alloy is much leaner than the previously proposed compositional range at which this decomposition process could occur. Further research is needed to expand the evidence base for this area of contention.

This chapter is a study of the microstructures found in Ti-15 wt.%Mo when heated at a range of temperatures for extended periods of time. This was to gain a general understanding of the system at equilibrium and to identify the critical techniques for characterising phase stability. Therefore, observations of heat-treated material were made using X-ray and electron diffraction and were compared to spatial observations as well as chemical measurements.

### 3.2 Methods

#### 3.2.1 Material and heat treatments

Material was received in the form of an 8 mm diameter bar supplied by Rolls-Royce plc. The composition of as-received material is provided in Table 3.1, giving a nominal composition of Ti-15 wt.%Mo. As prior thermo-mechanical treatment was unknown, the microstructure
3.2 Methods

Of the bar was reset by a one hour heat treatment at 800°C, approximately 15°C above the β transus temperature followed by a water quench. This bar was then cut into samples using a diamond saw and individual samples were encapsulated in separate glass tubes for long duration heat treatments. The samples were heat treated in box furnaces at temperatures that were independently checked using a thermocouple. The heat treatments conducted were those laid out in Table 3.2 and correspond to 500 hour exposures so that phase equilibrium could be achieved. Following the long duration heat treatment, the material was rapidly cooled to room temperature by immersion in cold water.

<table>
<thead>
<tr>
<th>Ti</th>
<th>Mo</th>
<th>Fe</th>
<th>O</th>
<th>C</th>
<th>N</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>84.26</td>
<td>15.56</td>
<td>0.01</td>
<td>0.13</td>
<td>0.01</td>
<td>0.01</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Table 3.1 Composition of the material studied (wt.%). Information supplied at the outset of the project by Rolls-Royce plc.

<table>
<thead>
<tr>
<th>Age Temperature (°C)</th>
<th>Age Time (Hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>500</td>
</tr>
<tr>
<td>400</td>
<td>500</td>
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<td>500</td>
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<td>600</td>
<td>500</td>
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<tr>
<td>700</td>
<td>500</td>
</tr>
<tr>
<td>800</td>
<td>500</td>
</tr>
</tbody>
</table>

Table 3.2 Thermal treatments investigated. After each treatment, the material was rapidly cooled by water quenching.

3.2.2 Sample preparation

Sections of the material from each of the heat treatment trials (according to Table 3.2) were cut into 8 mm diameter discs that were approximately 5 mm thick using a diamond saw. These coupons of material were cold mounted in epoxy resin to facilitate grinding using consecutively finer SiC paper. After grinding with grade 4000 grit paper, the surface of each of the resulting coupons was polished to a mirror finish using an activated colloidal silica solution. The final surfaces were flat and scratch free.

In addition to the preparation of the coupons, discs of material for examination using a transmission electron microscope (TEM) were electro-spark cut from each of the samples.
Heat treating Ti-15 wt.% Mo

heat treated at 300, 400, 500 and 700°C for 500 hours. These 3 mm discs were thinned using SiC paper to approximately 0.2 mm before final thinning to create electron transparent foils using a Struers twin-jet electro-polisher. The polishing solution used was 10% perchloric acid in methanol at a temperature of -35°C and was applied to the opposing sides of the material at a low flow rate and 18-20 V until a hole was produced at the centre. Regions adjacent to the hole were thin enough for TEM studies.

3.2.3 Scanning electron microscopy

The mounted coupons of material were imaged using a FEI Nova NanoSEM scanning electron microscope (SEM) operated at 20 kV. The images were taken using a back-scatter detector. Since heavier elements result in a higher proportion of back-scattered electrons, regions containing heavier elements appeared brighter. Differences in grain orientation can also cause contrast between two different regions with the same composition in a SEM image.

3.2.4 X-ray analysis

Phase determination was conducted using a Bruker D8 Advance theta/theta Cu X-ray diffractometer with a 0.2 mm Ni filter. X-rays were focused on the surface of each of the samples heat treated in Table 3.2 over angles between 30° and 90° 2θ. For each angle, the diffracted intensity was measured using the position sensitive detector. The samples were spun to maximise the number of illuminated grains in the X-ray beam. This ensured that for any given structure, all the peaks were located between 30° and 90° 2θ. The peak positions across this range were compared to a database of peak positions for the β, α and ω structures found in the National Chemical Database Service [159] to identify the phases present for each heat treatment temperature.

3.2.5 Transmission electron microscopy

Discs heat treated at 300, 400, 500 and 700°C for 500 hours were imaged using an FEI Tecnai Osiris scanning transmission electron microscope (STEM) operated at 200 kV with a high angle annular dark field (HAADF) detector. The HAADF detector was equivalent to the composition sensitive back-scatter detector found in an SEM, which meant brighter regions contained a higher average atomic number. In addition, to unambiguously determine
3.3 Long duration heat treatments in Ti-15 wt.%Mo

composition variation, energy dispersive X-ray (EDX) spectroscopy was conducted. Local composition measurements were performed using EDX mapping. The Ti-K and Mo-L signals were quantified at each pixel in the maps using the Gatan ESVISION software. During the quantification, a background was fitted followed by least-squares fitting of the data to a model. The predicted uncertainty depended on the length scale of mapping, but was no more than 1%. For each fit, the uncertainty was significantly smaller than the observed variation between precipitates.

Conventional transmission electron area diffraction was taken using a Jeol 200CX operated at 200 kV. Diffraction patterns were taken at the $<110>_{\beta}$ zone as this zone contained independent $\omega$ reflections. Foils from material heat treated at 800, 700, 400 and 300°C for 500 hours were imaged to give an overall indication of the key features.

3.2.6 Hardness

Vickers hardness was measured on the coupons of material for each sample in Table 3.2 using a macro-indenter with a square base pyramid tip and a force of 30 gN over a 30 s dwell. The indented square diagonals were measured using an eyepiece graticule and converted to a Vickers hardness using the nominal dimensions of the diamond tip. For each ageing condition, ten separate locations were indented across the coupon surfaces. The indents were separated by at least three times the diagonal to prevent one indent affecting a neighbouring indent.

3.3 Long duration heat treatments in Ti-15 wt.%Mo

3.3.1 Results

Representative backscattered SEM images of grain triple junctions across the 300°C to 800°C range are shown in Figure 3.1. The microstructure of Ti-15 wt.%Mo across the 300-800°C range consisted of equiaxed grains, approximately 75 $\mu$m in size. Samples treated at 800, 500, 400 and 300°C contained little contrast variation within each grain, Figure 3.1a & d-f which suggested that no large scale composition variation existed across the microstructure. Variation was observed between grains in Figure 3.1a & d-f due to beam channelling effects that occurred due to differing crystal orientations.
Fig. 3.1 SEM images taken using the backscattered electron detector of material heat treated for 500 hours at a range of temperatures.
Significant SEM backscattered (bs) contrast variation was observed for the ageing temperatures 700 and 600°C, Figure 3.1b & c respectively. At these two temperatures, Ti rich precipitates were located along the grain boundaries and within the grains. As commonly observed [23], the rejection of Mo from the grain boundary precipitates resulted in a higher concentration of Mo parallel to the boundaries which inhibited precipitation within zones adjacent to the grain boundaries. The morphology of the intra-granular precipitation had a plate appearance and 60°/120° orientation relationships between plates, closely matching a chevron appearance seen elsewhere [37]. Consequently, all of the precipitates shown in Figure 3.1b & c are entirely consistent with the α phase in a β matrix.

From previous studies of Ti-15 wt.%Mo, precipitates were expected to be observed in the 300-500°C ageing conditions [137]. However, no contrast attributable to precipitation was present in Figure 3.1d-f. This could have been because the precipitates were too small to resolve using an SEM. X-ray diffraction (XRD) from each of these conditions provided direct phase information. Offset scans of intensity against 2θ for each thermal treatment are plotted in Figure 3.2. The database peak positions for the α, β and ω phases are marked. It was found that many peaks contained contributions from multiple phases. Peak splitting, as a result of small differences in phase concentrations, was not sufficient to deconvolve the peak shape due to the additional presence of peak splitting from Cu-Kα1 and Cu-Kα2 contributions. In addition, despite reasonable grain statistics, due to the close correspondence between phases and the presence of residual processing texture, a full pattern Rietveld fit could not be achieved. Therefore, the volume fractions of the phases at each temperature could not be deduced. However, several peaks were found between 30° to 90° which contained intensity from only a single phase. These were predominantly used to identify the phases present at each temperature.

X-ray diffraction of a standard LaB₆ powder sample on this particular diffractometer showed the background between 30° and 90° 2θ was flat and the peaks were symmetric. The β peaks above the β transus at 800°C in Figure 3.2 were neither symmetric nor was the background flat. The presence of the β phase at each temperature in Figure 3.2 is the signature of a β titanium alloy. For example, the first three β peaks at 39°, 56° and 71° correspond to the {110}β, {200}β and {112}β respectively. However, each of these β peaks has a leading peak edge which cannot be attributed to the diffractometer. In addition, the asymmetry is not due to Cu-Kα1 and Cu-Kα2 contributions. This is because whilst Cu-Kα2 should contain half the intensity of Cu-Kα1, Cu-Kα2 is always found at higher angles. The peak asymmetry is therefore indicative of a second phase in addition to the β phase. Furthermore, there is a
Fig. 3.2 XRD phase analysis of material heat treated for 500 hours at a range of temperatures.
slight bump in the background intensity at 79°C which is the same location as the ω peak at 300 and 400°C. Therefore, the diffuse bump and the similar peak shape between 800°C and 300°C peak shape is a suggestion that ω is present above the transus temperature after a 500 hour thermal exposure.

As can be seen in Figure 3.2, co-occurring phases can generate overlapping XRD peaks in some positions. However, independent peak locations were present for the α and ω phases so these precipitates could be identified at each of the ageing temperatures below the β transus. In the 700-500°C range, the precipitate phase was the α phase. Whereas, at 300°C, the precipitate was the isothermal ω phase. Interestingly, at the intermediate temperature, 400°C, both α and isothermal ω were observed to exist together, with the ω peaks significantly sharper than at 300°C. This indicates that both the metastable ω and stable equilibrium α were present after 500 hours, which suggests either diffusion of Mo at 400°C is very slow or an equilibrium was achieved between the two phases.

The presence of the ω phase in the β matrix was studied by looking at the β grains in a TEM. For direct phase information, the back focal plane was imaged because it shows Bragg diffraction intensity that is complimentary to XRD data. Figure 3.3 contains diffraction patterns taken using photographic paper, which is very sensitive to diffuse intensity. The spots represent regions of constructive interference and correspond to diffraction planes. Diffraction patterns were taken following heat treatments at 800, 700, 400 and 300°C, Figure 3.3a-d. In the case of Figure 3.3b, the area imaged was specifically selected to represent only the enriched β matrix and therefore does not contain reflections from α precipitates. Within Figure 3.3a-d, primary β reflections were observed that corresponded to a <110>β zone. The {110}β, {200}β and {112}β reflections are indicated in part a. These three reflections are synonymous to those mentioned in the XRD data. Similar to the X-ray data, all of the β reflections contain contributions from an ω phase. This was not deduced by the asymmetry of the β reflections which was only slight. Instead, the ω phase can clearly be identified by intensity at 1/3 and 2/3 <112>β. Two variants were observed at each temperature in Figure 3.3a-d and are marked accordingly in Figure 3.3a for reference. The remaining two variants were contained within the primary β reflections. This was found by rotating to any <110>β zone and observing the same appearance in the diffraction pattern.

Additional reflections were found in samples heat treated to 400 and 300 °C which were not present in the samples heated to 800 and 700°C. These are marked with a "d" in Figure 3.3d and are located at 1/3 and 2/3 <110>β and 1/3 and 2/3 <200>β. It was observed that tilting
Heat treating Ti-15 wt.% Mo

Fig. 3.3 TEM [110]_β diffraction patterns from samples heat treated at a) 800°C, two ω variants are indicated b) 700°C, c) 400°C d) 300°C, additional reflections not seen at high temperatures (800 and 700°C) are marked.

away from the zone or imaging thinner material resulted in the disappearance of these reflections. The nature of this disappearance was attributed to double diffraction. Critically, double diffraction cannot occur in a single phase body centred cubic (BCC) structure. Therefore, the double diffraction must be linked to the ω phase and can only occur by the combination of two g-vectors, one from each of ω₁ and ω₂ variants. Since two variants of the ω phase are present in foils at each temperature treatment, double diffraction may also be present within the 800 and 700°C images. However, as the ω reflection intensities are significantly lower than at 400 and 300°C, they may not have been visible.

The primary difference between the ω reflections observed in the samples heat treated at 800°C - 700°C (Figure 3.3a and b) and 400°C - 300°C (Figure 3.3c and d) is the appear-
3.3 Long duration heat treatments in Ti-15 wt.%Mo

ance of the $\omega$ reflections. The $\omega$ reflections in the 800°C and 700°C conditions, which both contain quenched $\beta$ material, have a lower intensity and are streaked in the $<112>_{\beta}$ directions. As discussed in Chapter 2, this is characteristic of athermal $\omega$. In contrast, the $\omega$ reflections observed following heat treatment at a lower temperature of 400°C (Figure 3.3c) have greater intensity and are more symmetric. This is an indication that the $\omega$ phase present here is isothermal. This is also true of the sample heat treated to 300°C (Figure 3.3d). The diffraction spots in the 300°C sample were more diffuse than at 400°C. This difference may be explained by either the size or volume fraction of the phase precipitates. In order to establish the extent to which these factors were responsible for the differences observed it was necessary to directly observe the precipitates.

STEM annular dark field (ADF) imaging and EDX mapping were used to spatially resolve precipitates and provide information not available through diffraction data. ADF and chemical maps corresponding to the Ti and Mo EDX signal for 300, 400, 500 and 700°C ages are shown in Figure 3.4. For all the temperatures below the $\beta$ transus, Mo lean and Ti rich precipitates were deduced due to their dark appearance in the ADF images, the increase in signal in the Ti-K maps and the reduction of signal in the Mo-L maps. Critically, the shape and size of the precipitates was found to vary significantly between different heat treatment temperatures. In samples heat treated at 700 and 500°C the $\beta$ matrix contained precipitates that had a chevron appearance due to the presence of plates at 60° to each other. These precipitates were attributed to the $\alpha$ phase by their typical shape and orientation correspondence. In contrast, the ellipsoid precipitates in the 300 and 400°C samples were deemed the isothermal $\omega$ phase. A significant variation in precipitate size was found. For example, between the 300 and 400°C samples, and the 500 and 700°C samples the precipitate size changed by an order of magnitude between each step, Figure 3.4. This size effect may be the consequence of the diffusivity of Mo at different temperatures.

As the 500 hour heat treatments gave the Ti-15 wt.%Mo alloy sufficient time to achieve phase equilibrium, the equilibrium phase concentrations could be determined by EDX composition analysis of each phase. For each pixel in the EDX scans within Figure 3.4, the composition of the Ti and Mo were measured using the Ti-K and Mo-L excitations and the Gatan EVision database of Ti and Mo cross-sections. The array of composition values within each picture was then split into three categories of compositions relating to: 1) predominantly the precipitate, 2) predominantly the matrix and 3) unknown proportions of the precipitate and matrix confounded by volume effects. The latter case was more important for the precipitates, which were significantly smaller than the foil thickness. For example, if the precipitates are
Fig. 3.4 EDX-STEM chemical mapping of the Ti and Mo signal from thin regions of material which has been previously heat treated at the specified temperature for 500 hours.
Fig. 3.5 Quantitative precipitate and matrix composition measurements taken from Figure 3.4c, f, i and l.

very small, any measurements through the thickness of the sample will encompass several precipitates and regions of matrix and, therefore, only give the bulk alloy composition. The average composition and standard error for the matrix and precipitate phases are plotted in Figure 3.5a, along with the known allotropic temperature for pure Ti and the 774°C transus data point for Ti-15 wt.%Mo. Black dotted lines were drawn by eye to indicate possible phase boundaries. The red dotted line separates the measured compositions of the α and ω phases. For clarity, the lean portion of the diagram is re-plotted in Figure 3.5b. In this case, the solid black line is a linear interpolation between the known allotropic and bulk β transus Ti-15 wt.%Mo data points. All the data points in Figure 3.5a fall along equilibrium phase boundaries except the matrix composition for the 300°C aged condition. This is because the precipitates were too small and homogeneously distributed to define pure β regions. From Figure 3.5 the α and ω precipitates were found to be rich in Ti and contained less than 1 wt.% Mo. Interestingly, it was found that the composition of the isothermal ω precipitates was similar to the α composition. Extrapolating the β transus, Ti-Mo contains a fully stabilised β phase above 25 wt.%Mo.
Heat treating Ti-15 wt.%Mo

For β Ti alloys, precipitates are known to reinforce the ductile β matrix. To ascertain the strength improvements corresponding to α and ω precipitates, material from each heat treatment temperature was indented to measure the hardness. Large indents were applied to statistically average over several grains. Typical indents are shown in Figure 3.6. Indents in α containing microstructures, such as in Figure 3.6a, showed no deformation to the grains or surrounding material. In contrast, indents into ω containing regions (Figure 3.6b) often contained circumferential cracks surrounding the indent. This implied that the microstructures containing the ω phase were less ductile than those containing the α phase.

Table 3.3 contains a summary of the identified phases from SEM, XRD and TEM observations for each heat treatment temperature along with corresponding hardness measurements. The hardest microstructure was identified in material heat treated to 400°C where isothermal ω precipitates were dominant in the microstructure but evidence of the α phase (possibly located at the grain boundaries) was also observed in the XRD trace. In the samples heated at 300°C, which only contained isothermal ω precipitates, the microstructure was 100 Hv softer than the 400°C condition despite precipitates shown to be much finer. This is an indication that the α phase is important for high strength applications. The microstructure resulting from heating at 800°C, which contained athermal ω precipitates, was a further 100 Hv softer than the 300°C isothermal ω counterpart. Isothermal ω is therefore a better strengthen than athermal ω. Lastly, it was found that the heat treatments at 600°C and 700°C resulted in harder microstructures than material heated at 500°C despite all three containing predominantly α precipitates. In material heated at 500°C the α phase was most refined so an increase in hardness might be expected. However, when heat treatments were
carried out at higher temperatures of 700°C it was shown that the β matrix was sufficiently destabilised to also contain athermal ω, which further increased the hardness. From this, the presence of the ω phase appears to be more influential in increasing the strength of Ti-15 wt.%Mo than the refinement of the α phase.

<table>
<thead>
<tr>
<th>Ageing Temperature</th>
<th>From appearance in SEM</th>
<th>Phase ID from XRD</th>
<th>Phase ID from TEM</th>
<th>Vickers Hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>β</td>
<td>β</td>
<td>β+athermal ω</td>
<td>310 +/-3</td>
</tr>
<tr>
<td>700</td>
<td>β+α</td>
<td>β+α</td>
<td>β+α+athermal ω</td>
<td>248 +/-4</td>
</tr>
<tr>
<td>600</td>
<td>β+α</td>
<td>β+α</td>
<td>β+α</td>
<td>253 +/-2</td>
</tr>
<tr>
<td>500</td>
<td>β</td>
<td>β+α</td>
<td>β+α</td>
<td>216 +/-4</td>
</tr>
<tr>
<td>400</td>
<td>β+ω</td>
<td>β+ω</td>
<td>β+isothermal ω</td>
<td>498 +/-9</td>
</tr>
<tr>
<td>300</td>
<td>β+ω</td>
<td>β+ω</td>
<td>β+isothermal ω</td>
<td>410 +/-9</td>
</tr>
</tbody>
</table>

Table 3.3 Phases identified from SEM, XRD and TEM with corresponding hardness measurements.

3.3.2 Discussion

Employing a range of characterisation techniques is vital to identifying phase stability in β titanium alloys. From Table 3.3, three different deductions of phase stability could be made from the SEM, XRD and TEM data. This is partly due to the length scale of observed precipitates, Figure 3.4, and the limitations of each of the techniques to capture all of the information. However, the work presented in this chapter showed that on a nm to µm length scale, the β phase was observed to decompose to the athermal ω, isothermal ω and α phases during thermal treatments in the 300-800°C range. Critically, a single β phase was not found after a 500 hour exposure at 800°C and rapid cooling to room temperature. Interestingly, following heat treatments at 800°C (above the β transus) and 700°C (below the β transus) the ω phase was observed in the β matrix. At these temperatures, the ω is deemed athermal as no composition segregation could be related to the ω phase despite the high temperatures and times given for Mo diffusion to occur. It is not clear from these results whether the athermal ω is present at these high temperatures or induced from rapid cooling. In contrast, the ω phase found following heating at 300 and 400°C was distinctly isothermal. In particular, despite the lower temperature to the athermal ω condition, significant composition partitioning occurred.
Despite 60 years of research, the binary phase diagram for Ti-Mo is still disputed [6, 21, 116, 126, 156]. Recently, nano-scale spectroscopy was conducted on metastable $\beta$ alloys to establish solute redistribution [2, 12, 38, 39, 46, 66]. Primarily, atom probe tomography and high resolution (HR)-HAADF imaging was used for this purpose [67, 105, 106]. However, chemical quantification between parent and precipitate was not realised. EDX, is a well established tool for chemical mapping in SEM. However, this technique was unable to spatially resolve the $\omega$ phase or chemically map the phases. The use of EDX in a STEM enabled composition to be mapped on a nano-length scale using well established analytic techniques [160]. Here, for the first time in Ti-15 wt.%Mo, the chemical composition of the product phases after long thermal treatments was measured using STEM EDX to ascertain the equilibrium phase diagram (Figure 3.5). In agreement with previous studies [21], the $\alpha + \beta$ phase field was found to be between 0.8 wt.%Mo and 25 wt.%Mo. However, it was also found that the $\omega$ phase contained less Mo than previously reported [30, 64], with the equilibrium concentration being similar to that of the stable $\alpha$ phase rather than the reported 4 wt.%.

This is not unreasonable as both structures share hexagonal symmetry and consequently the same affinity to BCC Mo. The difference may be explained by the ageing times used. This study used a heat treatment time which was a factor of 100 times longer than in other studies [30, 64].

Between 400°C and 774°C stable equilibrium $\alpha$ was found, Table 3.3. Classically, the formation of the $\alpha$ phase is believed to follow a nucleation and growth model, with the $\alpha$ phase nucleating with equilibrium structure and composition [23]. Recent reports on finely distributed $\alpha$ suggest a non-classical homogeneous formation mechanism [115]. In this non-classical model, the $\alpha$ phase can have a composition deviating from the equilibrium composition and form by a pseudo-spinodal route whereby the two energy curves for the $\beta$ and $\alpha$ phases act like a single $\beta$ curve with a double well. The fine scale alpha observed at 500°C in this study is consistent in appearance with the previously reported intra-granular pseudo-spinodal $\alpha$ [115, 161]. However, the composition of the fine $\alpha$ plates was shown to be similar to the equilibrium composition of large alpha plates formed at 700°C, Figure 3.5, and there was no evidence at any temperature for non-classical precipitation. The only deviation from equilibrium was seen in the 300°C aged sample. However, in this case, the deviation was rationalised by the high volume fraction of small precipitates skewing the matrix measurements.
Isothermal $\omega$ is considered a non-equilibrium phase that is metastable [22]. However, a 500 hour thermal treatment is a substantial time to allow the formation of equilibrium phases, even below 500°C [22, 30, 137, 162, 163]. Therefore, as isothermal $\omega$ persisted over this period, the energy barrier for $\alpha$ in an $\omega$ microstructure must be significant and may impede future alloy design strategy [14]. For example, it may be too challenging to refine the $\alpha$ phase using the $\omega$ phase whilst ensuring all of the $\omega$ is removed. Furthermore, it has been previously assumed that the refinement of the $\alpha$ phase will result in an alloy of greater strength. In all cases, a lower $\alpha$ thermal treatment resulted in a finer microstructure, possibly due to the smaller distance over which diffusion can occur. However, from Table 3.3 and Figure 3.4, the microstructure containing fine $\alpha$ precipitates formed during a 500°C age was not as hard as the larger $\alpha$ precipitates observed in samples thermally exposed at 700°C, despite the fact that the $\alpha$ was smaller. Critically, the presence of athermal omega significantly outweighed the influence from the refinement of the $\alpha$ phase. Therefore, improving the understanding of the formation and nature of the athermal $\omega$ phase will be pivotal to strength improvements in Ti-15 wt.%Mo. This is the topic of the following experimental chapter.
3.4 Chapter conclusions

The aim of this chapter was to establish phase stability in the Ti-15 wt.%Mo binary by conducting 500 hour ages at a range of temperatures across the \( \alpha + \beta \) phase field followed by analysis using SEM, TEM, STEM with complementary spectroscopy. The following conclusions are made:

1) Different techniques produced different results. The results were not conflicting, but each technique contained limitations. For example, STEM imaging detected \( \omega \) precipitates and super-refined \( \alpha \) that were not resolved in an SEM. However, the STEM images did not sample as large an area as an SEM and possibly missed grain boundary \( \alpha \) precipitates which may have been observed in XRD. Both SEM and STEM enabled a spatial and composition analysis (by EDX) whilst the XRD and SADP did not. In contrast, XRD and SADP diffraction eluded to subtle differences between the isothermal and athermal \( \omega \) precipitates.

2) The \( \omega \) phase was present after 500 hours in the 300-800\(^\circ\)C range. Athermal \( \omega \) was found within the \( \beta \) phase quenched from 700 and 800\(^\circ\)C following 500 hour thermal treatments. Isothermal \( \omega \) was observed at 300 and 400\(^\circ\)C. In general, the isothermal \( \omega \) reflections were more symmetrical, sharper and included the presence of double diffraction. Critically, the presence and type of the \( \omega \) phase was the more influential with respect to hardness changes than \( \alpha \) refinement.

3) No evidence was found for a spinodal decomposition. All precipitates observed appeared to have followed a classical nucleation and growth process. However, a significant variation in precipitate size was found with temperature, suggesting diffusion of Mo in Ti is sluggish. Specifically, the smallest precipitates resolved were detected at 300\(^\circ\)C whilst the largest were at 700\(^\circ\)C.

4) The isothermal \( \omega \) precipitates shared a similar composition to the equilibrium \( \alpha \) precipitates. Whilst this was rationalised by the two phases sharing a hexagonal structure, this is contradictory to previous studies which showed compositions in the 4-7 wt.% range. However, the ageing times in this study were significantly longer than those reported elsewhere.
Chapter 4

The $\beta$ quenched condition and the athermal $\omega$ phase

4.1 Introduction

Additions of transition metal elements to Ti are known to stabilise the high temperature $\beta$ phase, enabling its metastable retention at room temperature following rapid cooling. However, such material is often reported to contain the $\omega$ phase, which forms through the collapse of consecutive pairs of $\{111\}_\beta$ [22, 30, 89]. This plane collapse does not contain a habit plane and therefore, is not a martensitic transformation. Instead, it is thought that the parent $\beta$ phase could have a soft phonon mode with respect to $\{112\}_\beta$ shear [164] and that the $\omega$ phase, which is present following rapid cooling, should be compositionally indistinct from the parent matrix at the point of quenching. However, at present there is conflicting evidence suggesting that a chemical alteration accompanies the structural modification [6, 69]. Thus, determining the mechanism of $\omega$ formation remains an intriguing question.

The nature of the athermal $\omega$ transformation has been studied extensively using lattice imaging in a transmission electron microscope (TEM) [85, 98–101, 165]. However, phase contrast effects prevented early studies from directly imaging the $\{111\}_\beta$ collapse [99] and compositional information was unobtainable due to the dominance of elastically scattered electrons [5]. Improved atomic column resolution and contrast have been achieved by sampling only the incoherently scattered electrons using a high angle annular detector in a scanning transmission electron microscope (STEM) [5, 6, 86]. Recently, interest in the $\omega$ phase and its effect on subsequent phase transformations [41, 150, 166–170] has led to new
The $\beta$ quenched condition and the athermal $\omega$ phase

observations through high angle annular dark field (HAADF) imaging [5, 67, 105, 106].

HAADF images taken from $\beta$ quenched Ti-18 wt.%Mo and Ti-5Al-5Mo-5V-3Cr (wt.%) showed intensity variations over a 5 nm wavelength [5, 131]. As incoherent scattering is related to composition, the variation was deemed to originate from differences in the local chemistry. Therefore, the intensity modulations were attributed to a spinodal decomposition of the $\beta$ phase. Consequently, a novel mixed-mode theory for the athermal $\omega$ transformation was developed based on this spinodal decomposition [115].

Furthermore, HAADF images of Ti-5Al-5Mo-5V-3Cr (wt.%), have shown intensity variations on an atomic length scale, with the collapsing planes exhibiting a lower intensity than the non-collapsing planes [106]. This intensity difference has been attributed to variations in the average atomic number of each column of atoms, which suggests preferential site occupation and, possibly, ordering within the $\omega$ phase. Intensity variations between the collapsing and non-collapsing planes have also been observed in rapidly cooled Ti-18Mo (wt.%) [5]. Similarly, tri-layered structures have been reported in Gum metal (Ti-31.9Nb-2.0Ta-2.7Zr-0.3O wt.%) when imaged under HAADF conditions [105]. However, multi-slice scattering simulations suggest that the observed intensity variations could also be related to the structural modification of the $\omega$ phase rather than compositional effects [86, 105]. To date, no compositional data directly related to a tri-layer $\omega$ HAADF feature has been presented, without which it is impossible to ascertain the source of the observed intensity variations.

In this chapter, the tri-layer periodicity of $\omega$ precipitates within Ti-15Mo (wt.%) has been studied using HAADF STEM imaging coupled with electron energy loss spectroscopy (EELS). First HAADF images were used to investigate the $\beta$ and athermal $\omega$ phases for evidence of spinodal decomposition following rapid cooling. Having found no evidence supporting the novel mixed-model transformation, the possibility of local structure was investigated. The data suggest that the tri-layer intensity variations are not related to preferential site occupation but are the result of the imaging conditions within the microscope. This provided a useful tool for understanding the structural nature of the athermal $\omega$ phase.
4.2 Methods

4.2.1 Material

A rolled bar of Ti-15 wt.%Mo was supplied by Rolls-Royce plc. Sections of this bar were encapsulated in quartz glass ampoules under an argon atmosphere and heat treated for one hour at either 785°C, 875°C, or 975°C; 10°C, 100°C or 200°C, above the \( \beta \) transus temperature. After the heat treatment, the material was rapidly cooled by water quenching. Material quenched from above 775°C is regarded as the starting condition or as the quenched condition that many \( \beta \) Ti alloys are subjected to prior to ageing. Electron transparent samples were produced by twin jet electropolishing using a solution of 8% perchloric acid in methanol at -35°C and 18V.

4.2.2 Electron microscopy

Electron lattice imaging was conducted using an FEI Titan3 STEM with multiple nested annular dark field (ADF) detectors, which enabled the simultaneous acquisition of images at different inner collection angles. The microscope was operated at 300 kV and was aberration corrected to achieve atomic resolution for both low and high angle annular dark field images, LAADF and HAADF respectively. The inner collection angle for low angle annular dark field (LAADF) was 26.0 mrad. The inner collection angle of the HAADF detector was varied by changing the camera length through controlling the post sample lenses. Camera lengths of 145, 115, 91 and 73 mm were used, which corresponded to inner collection angles of 39.0, 49.0, 62.6 and 79.6 mrad.

Raw images are those which have not been post processed more than minimal brightness and contrast adjustments. All of the images shown in this chapter are raw unless described as filtered. Images that were processed, were filtered using one of two common HAADF filtering methods. The first, most extreme method was performed in ImageJ software and utilised a bandpass filter to remove high and low frequencies in the image. The second approach, involved the average background subtraction (ABS) procedure in Digital Micrograph [171], which removes the amorphous components and enhances periodic features [172]. Whilst the first method effectively normalises global contrast variations and smooths atom appearances, the second method suppresses background noise which might result from surface carbon contamination.
Simultaneous ADF imaging and EELS were conducted in the same microscope using a high resolution Gatan 865 Tridiem spectrometer. Electron loss energies in the range of 200 to 700 eV were mapped using a 0.5 Å step size and 0.02 s dwell over regions containing both β and ω phases. Local composition was determined by integrating background corrected post Ti L2,3 edge intensities over a 100 eV range for each pixel in the map. To suppress background noise further, the Ti L2 (462 eV) and L3 (456 eV) edges were isolated using a Poisson noise decomposition and a blind source separation in HyperSpy [173, 174] to enable the relative level of Ti atoms in the sampled columns to be displayed as a function of position.

4.2.3 Simulations

A schematic representation of a STEM instrument equipped with multiple detectors is shown in Figure 4.1. Mathematically, this microscope setup can be simulated by dividing the region of interest into single layers of atoms separated by vacuum. A wave function representing the accelerated electrons is transmitted and propagated through each of these slices at every point in the image. At each point the exit wave function is Fourier transformed to simulate a convergent beam diffraction pattern incident on an annular detector. Through integrating the function over several annular ranges, different detectors can be simulated [107].

As with all modelling and simulating techniques, several approximations are necessary. Here, the weak phase approximation is used. This is when the effective scattering of the incident function on the potential is small, and therefore the plane wave will only suffer a phase change. This technique does not include multiple scattering events or account for the curvature of the Ewald sphere.

Simulated LAADF and HAADF images were produced via a multi-slice approach using stemslic [175]. The microscope conditions that were used in the models were 300 kV, an objective aperture of 19.5 mrad and a defocus of 1 nm. Defocuses of 10 nm and 20 nm were also considered but produced no significant differences to the simulations using a 1 nm defocus. For atom clarity, the lenses were treated as ideal with no aberrations. The exit waves were integrated between angles of 20 and 80 mrad to approximate the experimental LAADF condition, and between 80 and 300 mrad for the HAADF condition.

A total of 52 layers of Ti atoms were used in the simulations, giving a foil thickness of 12 nm. For each layer, the program atompot [107] was used to create projected atomic potentials with which the electron wave functions interacted. Three distinct descriptions of the β and ω
4.2 Methods

Fig. 4.1 Schematic representations of a STEM equipped with multiple detectors and how it can be simulated using a multi-slice technique.

structures were simulated; i) perfect $\beta$ and ideal $\omega$ separately, ii) perfect $\beta$ interspersed with 8% ideal $\omega$, similar to the approaches used by Sankaran et al. [105] and Sukedai et al. [100] and iii) $\beta$ with a frozen phonon description of the $\omega$. The frozen phonon description allowed each collapsing atom to have any position between the perfect $\beta$ and ideal $\omega$ structures determined by a Weibull probability function with shape parameter of 3 and scale parameter of 1.
4.3 On the $\beta$ quenched condition in Ti-15 wt.%Mo

4.3.1 Results

Figure 4.2 is a representative high resolution HAADF image of quenched Ti-15 wt.%Mo that contains atom columns imaged down $<110>_{\beta}$. The data is considered raw as no post processing to the image was applied after acquisition, which means atom column intensity is directly interpretable. Critically, within Figure 4.2, there are no regions of atom columns that contain significantly larger intensities than any other regions. As such, no periodic intensity variations were observed that could be explicitly linked to a spinodal decomposition.

Figure 4.2 contains atom columns in a regular rectangular array comparable to Figure 4.3, which is a projected view of two overlaid body centred cubic (BCC) supercells, one black and one blue, viewed down a $<110>_{\beta}$ zone. This is because the electrons incident on the HAADF detector have passed through the thickness of the material and interacted with atoms at each layer. By measuring the distance between alternate atom columns, the lattice parameter was determined to be $3.3 \text{ Å} (\pm 0.1 \text{ Å})$, which is close to the lattice parameter of pure Ti but higher than the expected value of $3.26 \text{ Å}$ for Ti-15 wt.%Mo. The difference between the expected and determined lattice parameters may be a calibration issue or could be accounted for by the quench condition not solely containing the $\beta$ phase. For example, metastable $\beta$ alloys can also contain the athermal $\omega$ phase and possibly a spinodal decomposition. Additional structures through the thickness of a foil will alter the path of electrons and will affect the apparent location of atom columns. However, before the inherent material factors on atom column positions are considered, the external microscope effects on the raw image must be accounted for.

Within Figure 4.2 the effects of sample drift, scanning coil feedback error, probe noise and probe aberrations can be corrected using post image acquisition processing. An established post processing method is to remove high and low frequency information from HAADF images using a bandpass filter. As many of the external microscope effects are either high or low frequencies, a bandpass filter will clean an image. For example, sample drift and coil feedback errors are seen as distortions with a low periodicity across the image. The image was acquired by rastering the electron probe across the region of interest. Therefore, two pixels in horizontal scanning direction are acquired closer in time to neighbouring pixels in the vertical direction, resulting in a positional error that is only apparent over wide spacings in the vertical direction where the error is compounded. Similarly, coil feedback error is apparent across the horizontal width of the image and is due to the coils which control the
Fig. 4.2 Raw HAADF STEM image along $<110>_{\beta}$ taken from material thermal heat treated at 785°C, followed by rapid cooling.
scanning probe not correctly locating the scanning probe to the beginning of subsequent lines. Probe noise and probe aberrations are high frequency distortions in HAADF high resolution (HR)-STEM images as they affect the shape of the atom columns, causing a deviation from an ideal 2D Gaussian shape. Figure 4.4 has been generated from Figure 4.2 by applying a bandpass filter to remove high and low image frequencies. Figure 4.4 contains smoother atom column appearances and a more normalised global background level. However, despite the fact that the contrast is more apparent after processing in Figure 4.4 than in Figure 4.2, no regions of higher or lower contrast could be distinguished and described as spinodal. In addition, the post processing did not remove the atom column distortions, suggesting these are not simply due to microscope error and, therefore, require further investigation.

Whilst it may appear that the distortions in Figure 4.2 and Figure 4.4 are random, localised \{111\}_\beta collapse can be identified. Typically, \(\beta\) quenched material is reported to contain the athermal \(\omega\) phase, which is observed as diffuse 1/3 and 2/3\(<112>\)_\(\beta\) reflections in a \(<110>\)_\(\beta\) selected area diffraction pattern (SADP) obtained in a conventional transmission electron microscope (CTEM). A frequency map of an atom column image is equivalent to a conventional diffraction pattern. The frequency map can be obtained by a fast Fourier transform (FFT) of the raw image and subsequent shifting of the low frequencies to the centre in addition to applying four fold symmetry. The central region of a shifted Fourier
Fig. 4.4 Filtered HAADF HR-STEM image along \(<110>\beta\) taken from material thermal heat treated at 785°C followed by rapid cooling. A bandpass filter has been applied to remove high and low frequencies.
The $\beta$ quenched condition and the athermal $\omega$ phase transform of Figure 4.2 is given in Figure 4.5a. This image is analogous and similar to the conventional SADP along a $<110>_{\beta}$, and highlights the presence of both $\omega$ variants and the resulting $\{111\}_{\beta}$ distortions within the HAADF image. Therefore, HAADF STEM images at this magnification contain features that are representative of larger areas of material.

![FFT Beta Variant 1 Variant 2](image)

Fig. 4.5 The central region of a shifted fast Fourier transform of Figure 4.2 over a) the entire image and sub sections of the image containing b) $\beta$ with no $\omega$ reflections, c and d) $\omega$ variants 1 and 2 present within the $<110>_{\beta}$ zone.

In the spinodal description of athermal $\omega$ formation, the reported size of $\omega$ containing regions is on the same length scale as the composition fluctuation, approximately 5 nm [5]. Within these regions, collapse of the $\beta$ structure to the $\omega$ structure is thought to occur due to a lower concentration of $\beta$ phase stabilisers. No composition fluctuations were observed in Figure 4.2 and Figure 4.4, so a different method for locating the $\omega$ phase had to be employed. Three 5 nm x 5 nm sub areas in Figure 4.2, indicated by boxes labelled variant 1, variant 2 and beta, were isolated by image cropping and independently Fourier transformed, Figure 4.5 b-d, to
show local phase information. The Fourier transform of an area containing no distinct $\omega$ reflections is shown in Figure 4.5b. The rectangular array of maxima in frequency space are consistent with the expected SADP of a single $\beta$ phase when viewed along the $<110>_\beta$.

In contrast, the Fourier transform of a region containing $\omega$ reflections is shown in Figure 4.5c. As with Figure 4.5b, a rectangular array of frequency maxima can be observed. In addition, weaker maxima can be seen at 1/3 and 2/3 of one of the $<112>_\beta$ directions only, which indicate the presence of a single variant of the $\omega$ phase. Similarly, the second $\omega$ variant that can be distinguished within any $<110>_\beta$ zone can be observed in Figure 4.5d. This Fourier method is therefore useful in spatially resolving phase information within a HAADF image and is used in later figures to identify $\omega$ containing regions.

For ease of comparison between the $\beta$ and $\omega$ structures, the BCC unit cell can be re-defined as a hexagonal cell. Figure 4.6 is a supercell of atoms, shown in blue, with the $\beta$ structure and highlights how the BCC unit cell is related to the hexagonal unit cell. The atoms contained within each of the unit cells are coloured black. Whereas the BCC cell contains two atoms per cell, the hexagonal cell contains three. The displacement component of the $\beta$ to $\omega$ transformation is understood to be the connective collapse of 2/3 of the $\{111\}_\beta$. Within one hexagonal unit cell, two of the three atoms relocate in the $<111>_\beta$ direction. This is best observed along $<110>_\beta$, Figure 4.7, where the one corner blue atom remains stationary and the two black atoms displace. Perfect $\beta$ is where the atoms are all in the $\beta$ phase and are directly located on their lattice sites. Of course, in real material, this will only occur at 0°C due to the effect of thermal vibrations. However, the appearance of an atom column in HAADF images is the average of all the atoms within the atom column, which will average the thermal effects. Therefore, the atom column location will tend to or be close to the perfect $\beta$ locations. The ideal $\omega$ structure is when the displaced atoms shift by $1/6a\beta$ in the $<111>_\beta$ direction such that the atoms are located at the $1/3,2/3,1/2$ and $2/3,1/3,1/2$ positions. Where collapse is incomplete, the unit cell can be described as trigonal.

Incoherent high resolution imaging can directly observe the $<111>_\beta$ collapse. Figure 4.8 contains high magnification raw HAADF images taken from a $\beta$ containing region and an $\omega$ containing region. In each case, the perfect $\beta$ and ideal $\omega$ locations are overlaid by black circles. Critically, within the $\omega$ containing region, the atom collapse is incomplete. The dotted lines marked 1 and 2 indicate two ideal $\omega$ positions in adjacent unit cells. In both cases, the centroids of the displaced atom columns do not lie directly on the line. Interestingly, the atom column positions relative to the dotted lines are different between the two lines and
The $\beta$ quenched condition and the athermal $\omega$ phase

Fig. 4.6 A supercell of blue atoms with a BCC structure. A BCC unit cell and an equivalent hexagonal unit cell are drawn. Black atoms are those defined by the drawn BCC and hexagonal cells respectively.
4.3 On the $\beta$ quenched condition in Ti-15 wt.%Mo

![Diagram of Perfect Beta and Ideal Omega Structures](image)

Fig. 4.7 The three atom hexagonal unit cell when viewed along $<110>_{\beta}$ showing the atom locations for the perfect $\beta$ and ideal $\omega$ structures. In the transformation from $\beta$ to $\omega$, the blue atoms remain stationary whereas the black atoms collapse along the $<111>_{\beta}$.

When two atoms are compared along one line. These observations are typical across all of the HAADF images taken in the $\beta$ quenched condition. However, no conclusions can be made as to the extent of collapse within the athermal $\omega$ phase towards the ideal $\omega$ structure. This is because it is not known if any of the $\beta$ phase is also contained in atom columns which have shifted along $<111>_{\beta}$. Therefore, incomplete collapse could be an effect of averaging between the perfect $\beta$ and ideal $\omega$ structures.

Figures 4.2 and 4.5a are from material quenched approximately $10^\circ$C above the $\beta$ transus temperature. This temperature was selected since the critical point for miscibility in the $\beta$ phase field would be at a low temperature rather than a high temperature. It may be possible that the critical temperature is below the $\beta$ transus, however, any composition segregation would be attributed to the $\alpha$ phase. As no evidence for spinodal decomposition was found at $10^\circ$C above the $\beta$ transus temperature, it was decided to explore material quenched from higher temperatures. This is because the higher temperatures may aid any composition fluctuations which could lead to separation. Therefore, material was quenched from $875^\circ$C and $975^\circ$C, which are approximately $100$ and $200^\circ$C above the $\beta$ transus. Raw HAADF images and their respective Fourier transforms at $785^\circ$C, $875^\circ$C and $975^\circ$C are shown in Figure 4.9. Whereas, no global intensity variation was observed at $785^\circ$C, differences in raw HAADF intensity within the image were found at $875^\circ$C and $975^\circ$C, Figure 4.9. However, the intensity variation did not correspond to $\beta$ peak splitting in frequency space. Therefore, the intensity variations could not be attributed to a spinodal decomposition. Instead, it is suggested that the observed intensity variations are likely to be thickness effects from non-flat foils rather than as a result of differences in composition.
The β quenched condition and the athermal ω phase

Fig. 4.8 High magnification regions of a raw HAADF image that contain atom columns with a) the β structure and b) the ω structure. The perfect β and ideal ω structures are overlaid. The two dotted lines (1 and 2), drawn in adjacent unit cells, indicate that the observed collapse can vary depending on the region selected.
4.3 On the $\beta$ quenched condition in Ti-15 wt.%Mo

Fig. 4.9 Raw HAADF images and the equivalent reduced Fourier transform for three $\beta$ heat treatments.
4.3.2 Discussion

High resolution TEM images are difficult to interpret without a comprehensive understanding of the system. This limited early HR studies of the ω phase [98, 100, 101]. In contrast, HAADF imaging is incoherent and contains a Z dependence, thereby enabling simultaneous observations of structure and composition. In previous studies, which reported raw and Fourier filtered HAADF HR-STEM images of Ti-18 wt.%Mo cooled from the β phase field, distinct ω containing regions were observed within regions of lower local intensities, Figure 4.10 [5, 6]. These were attributed to fluctuations in the Mo content and were taken as evidence of a spinodal decomposition of the β phase [6]. Critically, these images are comparable to the raw and filtered HAADF images in Figure 4.2 and Figure 4.4 since they were acquired in similar HAADF HR-STEM machines at approximately the same magnification and both along the same zone. Despite this, no evidence for a spinodal decomposition was found in this work. Therefore, the differences between experimental results are potentially due to 1) alloy composition and prior processing, 2) quench temperature, 3) hold time 4) cooling rate, 5) sample preparation, 6) microscope setup and 7) post processing effects. These seven factors are discussed below.

A β phase miscibility gap is a possibility [118–120] and is tentatively included on the Ti-Mo binary phase diagram [116]. Accordingly, the β phase in both Ti-15 wt.%Mo and Ti-18 wt.%Mo would spinodally decompose. However, the spinodal was only reported in Ti-18 wt.%Mo [5, 6] and not observed in this work. Whilst these two alloys could be separated by a phase boundary, they are only 3 wt.%Mo different. Alternatively, the initial microstructure of either alloy could be inhomogeneous due to composition segregation as a result of casting. The aim of a β solutionising step is to allow homogenisation of the microstructure. In this study, material was homogenised for an hour, twice the time allowed by Devaraj et al. [5]. However, both materials came from commercial feedstocks which means they probably also have typically had thermo-mechanical and recrystallisation heat treatments to remove any macro or micro-segregation from casting.

It is reasonable to assume that the non-equilibrium spinodal phase field is within the equilibrium α + β phase field, as a spinodal would not occur in the single phase stable β phase field. This is significant as the composition separation in Ti-18 wt.%Mo, Figure, 4.2, must have happened during the quenching process. In this work, material was rapidly cooled by water quenching. Whilst the exact cooling rate is unknown as the process was uncontrolled, the temperature of the material reached room temperature within a few seconds. In fact, no diffusion was evident from higher quench temperatures, Figure 4.9, where a higher temperature
4.3 On the $\beta$ quenched condition in Ti-15 wt.%Mo

Fig. 4.10 Raw and filtered HAADF images taken along $\langle 110 \rangle_\beta$ showing a variation in contrast which is attributed to $Z^2$. Taken from [5].
would require more time for heat loss and therefore a slightly slower quench. Material in Figure 4.10 was quenched from a similar temperature, within 15°C of the highest treatment here, Figure 4.9e. However, a significant difference is that the material depicted in Figure 4.10 was rapidly cooled by argon flow within the furnace, yielding a cooling rate of 10°C/s [5], significantly slower than in these experiments. This means diffusion might have occurred and therefore, the composition variation observed could be from the formation of isothermal ω and not β phase decomposition.

The differences between Figure 4.2 and Figure 4.10 may be the result of sample preparation. In this work, the foils were electro-polished, which could lead to wedge shaped foils around the hole edge where the atom columns were imaged. Evidence for this is shown in Figure 4.9b and c, where background intensities varied linearly across the images since HAADF image intensity is sensitive to sample thickness. Ion milling can manufacture flat foils, however, they can also damage the surface by preferential milling and inducing surface strains. The material in Figure 4.10 was focused ion milled (FIBed), which uses Ga ions to mill the surface. FIB damage was recognised [176] and minimised by including a low kV 4-10 nanomill Ar cleaning step [177]. However, the probe at this step was very close to the 5 nm length scale of spinodal-type features observed. Therefore, despite HAADF imaging suppressing strain effects, the nanomill may have introduced enough strain to be observed.

The detector setup in the microscope could also affect Z sensitivity. Generally, an ADF detector is considered to be in the HAADF condition when the inner collection angle is at least three times the probe semi convergent angle. This ensures the signal is predominantly incoherent and Z dependent. Admittedly, the resolution of the microscope employed here was not as good as that used for producing Figure 4.10, having a probe semi-angle of 20 mrad compared to 17 mrad [5]. However, here, the inner collection angle of the HAADF detector was changed to 76 mrad by varying the power of the post sample lenses to ensure incoherency. The inner collection angle in Figure 4.10 is not known and, therefore, could be much larger, resulting in a greater Z sensitivity.

Lastly, whilst Figure 4.2 and Figure 4.10 both contain raw data, the intensity variation in Figure 4.10 is most apparent in the filtered image. Without a full description of the post processing steps, it is unknown if any filtering artefacts have been introduced, thereby reducing the impact of the results. In general, the novel-mixed mode mechanism was heavily weighted on one HAADF image. Here, several raw images were taken for different thermal treatments and, despite the similarity between the two studies, clear differences are apparent.
4.4 On the possibility of local structure in athermal $\omega$

4.4.1 Results

A raw, unfiltered, HAADF image of the as-quenched material along $[011]_{\beta}$ is shown in Figure 4.11a. The reduced FFT of this image is inset in the figure and provides analogous information to a conventional selected area diffraction pattern. In this case, the frequencies corresponding to the $\beta$ reflections have been circled, leaving additional signals at $1/3$ and $2/3$ of $[2\bar{1}1]_{\beta}$ and $[21\bar{1}]_{\beta}$. These frequencies correspond to the two variants of the $\omega$ phase that reside within any given $\{011\}_{\beta}$.

Lattice distortions corresponding to one of the $\omega$ variants can be seen within the region enclosed by the white box in Figure 4.11a. For clarity, this region is magnified in Figure 4.11b. The $\omega$ phase can be identified by a distortion of the $\{111\}_{\beta}$ with respect to the $[200]_{\beta}$ when compared to a perfect $\beta$ structure. An example of this is contained within the box in Figure 4.11b. The atomic shifts can be seen more clearly in Figure 4.11c, which is the same region as Figure 4.11b, following the application of an ABS filter to Figure 4.11a. With the removal of the amorphous background component, a systematic variation in atom column intensity can be observed, similar to the tri-layer periodicity reported previously in more compositionally complex systems [105, 106].

To visualise this tri-layer periodicity more easily, the intensity within the white boxes in Figures 4.11b & c, were summed as a function of the position along $[200]_{\beta}$. The intensity profiles of the boxes are presented in Figure 4.11d & e for the raw and ABS filtered data respectively. These plots show the summed intensity of seven atom columns, where atom columns 2 & 3 and 5 & 6 contain distortions consistent with the $\{111\}_{\beta}$ collapse associated with the $\omega$ phase. In both the raw and ABS filtered cases, the atom columns in positions 1, 4 and 7 have greater HAADF intensity than those in positions 2, 3, 5 & 6. These observations are entirely consistent with those in previous studies of Gum metal [105] and Ti-5-5-5-3 [106], which identified the tri-layer periodicity.
The $\beta$ quenched condition and the athermal $\omega$ phase

Fig. 4.11 a) A raw (unfiltered) HAADF image of as-quenched Ti-15 Mo (wt.%) from a [011]$_{\beta}$ zone including the corresponding reduced FFT (inset), b) magnified view of the region within the white box shown in part a, c) ABS filtered counterpart of part b, d & e) intensity profiles taken from within the same area as indicated by the boxes in parts b and c.
HAADF signal is predominantly a result of incoherent scattering and intensity variations are commonly attributed to the atomic number of the species within a given column, $Z^2$. As Mo has a higher atomic number than Ti, any preferential site occupation or ordering would be expected to give rise to localised regions of greater intensity. Based on this premise, the results presented in Figure 4.11 could be interpreted as the Mo atoms having a site preference in the $\omega$ phase, occupying the non-collapsing planes, i.e. those in positions 1, 4 & 7.

To determine the possibility of preferential site occupancy of the Mo atoms in Ti-15Mo (wt.%), EELS element mapping with simultaneous ADF imaging was conducted. Figure 4.12a contains an EELS spectra between 200 and 700 eV for an $\omega$ containing region of material. Ideally, to map the local concentration of Mo, the Mo M4,5 edge intensities would be used. However, as can be seen in Figure 4.12a, the Mo M4,5 edges at 300 eV are close to the carbon K edge, which is located at 284 eV [178]. Some surface carbon contamination is expected and, therefore, the Mo and C cannot be deconvoluted. Despite the Mo edge overlapping with the C edge, the relative concentration of Mo can still be deduced, as Ti-15Mo (wt.%) is a binary system, which means the Ti edges and Mo edges are intrinsically linked. Additionally, the Ti L2,3 edges at 462 and 456 eV exhibit sharp threshold peaks and allow background subtraction over a large post edge region. Therefore, the shaded area in Figure 4.12a is directly related to the concentration of Ti in the illuminated volume.

Figure 4.12b is an ADF image taken from the same region as Figure 4.11 and contains both the $\beta$ and $\omega$ phases. It is apparent in Figure 4.12b that the tri-layer intensity periodicity is present in the same orientation as the $\omega$ precipitate, with the less intense atom columns corresponding to those that are distorted. Figure 4.12c is the unfiltered image of the boxed region in Figure 4.12b with the first 7 atom columns numbered. Atom columns at positions 1, 4 & 7, which are the non-collapsing columns, have greater intensity than those at positions 2, 3, 5 & 6. The Ti concentration map, determined from the simultaneously acquired EELS spectra from the same region as Figure 4.12c is presented in Figure 4.12d. Significantly, the profile in Figure 4.12d, which is related to the Mo concentration, does not exhibit the tri-layer periodicity, as shown in its ADF counterpart.

The spectra in Figure 4.12a was also analysed in an alternative way to attempt to reduce to noise seen in Figure 4.12d. Instead of integrating beneath the Ti-edges, the data was deconvoluted using Hyperspy software into a series of components. Again, it was found too difficult to separate the C effects from the Mo component. However, the Ti component was successfully extracted. The Ti L2,3 edge component extracted from Figure 4.12a is shown in
Fig. 4.12 a) EELS spectrum for Ti-15 wt.%Mo over a 500 eV energy range. Major Mo, Ti and C edges are labelled. The shaded region indicates the post edge window that was integrated over, b) an ABSF ADF image along [011]$_\beta$ of an $\omega$ containing region which contains the atom column tri-layer periodicity. c) The raw ADF image from the white boxed region in part b with the box profile and first 7 atom columns labelled, d) The simultaneously acquired EELS map with the profile plotting the Ti L$_{2,3}$ signal along [200]$_\beta$. 

The $\beta$ quenched condition and the athermal $\omega$ phase
Figure 4.13 along with a Ti map of the imaged region, generated using this component.

Fig. 4.13 a) The Ti-L2,3 component extracted from Figure 4.12a using Hyperspy software, b) The resultant Ti map of the imaged region using only the deconvoluted Ti-L2,3 component.

Figures 4.14a & b show images that were acquired simultaneously from the ADF detector and the Ti L2,3 edge component of the EELS spectrum. Despite the imaging resolution being reduced to optimise the EELS signal, the atom columns are more clearly defined than in Figure 4.12d. Again, the tri-layer periodicity could still be seen in the ADF image and the corresponding box profile shown in Figure 4.14c. Whilst analysis of the EELS signal from the same box did show variations in Ti signal from each atom column, Figure 4.14d, these variations did not match the column intensities observed in the ADF image. Therefore, spectroscopy data does not support the idea that the intensity variations observed in Figure 4.11 are compositionally related.

Recently, Sankaran et al. [105] suggested that the structural alteration associated with the \( \omega \) transformation could give rise to the observed periodicity and demonstrated this by performing multi-slice HAADF simulations. A similar approach has been followed here, but the simulations have been extended to include signal from smaller inner collection angles, and therefore more elastic scattering, in addition to the structural modification.

Multi-slice ADF simulations were performed on two model structures. The first structure represented a perfect \( \beta \) material, where all atoms were located exactly on their ideal sites. The second structure corresponded to an \( \omega \) containing \( \beta \) material, simulated using a frozen
Fig. 4.14 a) A raw (unfiltered) ADF image showing the tri-layer structure, b) simultaneously acquired Ti EELS map, c) intensity profile taken from the box marked in part a, and d) EELS Ti signal taken from the box marked in part b.

phonon approach. Simulated ADF images, corresponding to low (20 mrad, LAADF) and high (80 mrad, HAADF) inner collection angles were calculated for these two structures using only Ti atoms. The resulting images, corresponding to the [011]_β zone, are shown in Figure 4.15. When considering a perfect β structure, Figure 4.15a & b, no evidence of tri-layer periodicity can be observed. This is unsurprising, as all of the atom positions are well defined and Figure 4.15b is consistent with that produced in Sankaran et al. [105].

In contrast, the simulated images for the β structure which has been distorted by the ω phase, Figures 4.15c & d, show intensity variations between atom columns in the collapsing and non-collapsing planes. Critically, the predicted intensity variation between the two sets of planes is reversed as the inner collection angle changes. This can be seen more clearly in the corresponding box profiles shown in Figures 4.15e & f. At low collection angles, Figure 4.15e, the collapsing planes i.e. numbers 2, 3, 5 & 6, have greater intensities than the non-collapsing planes, 1, 4 & 7. Conversely, at higher collection angles, Figure 4.15f, the collapsing planes have lower intensities than the non-collapsing planes. This latter simulation is equivalent to the experimental data presented in Figure 4.11 and Figure 4.14, albeit without accounting for any aberrations in the microscope.
4.4 On the possibility of local structure in athermal $\omega$

Fig. 4.15 Multi-slice simulations of the perfect $\beta$ phase structure in a) LAADF and b) HAADF imaging conditions. The modified $\beta$ phase structure under c) LAADF and d) HAADF imaging conditions. Intensity profiles corresponding to e) the LAADF simulation (white box in part c) and f) the HAADF simulation (white box in part d).
The simulated HAADF result for the $\beta + \omega$ structure is consistent with the work of Sankaran et al. [105]. This similarity is interesting as the previous model incorporated discrete layers of a modified $\beta$ structure to represent the $\omega$ structure, whereas a frozen phonon approach has been used here. This suggests that any deviation in atom positions, away from the ideal $\beta$ structure, can influence the atomic column intensity observed in ADF images. To explore this further, in the present study this analysis was extended to include scattering at smaller inner collection angles.

Using the nested annular detectors in the Titan microscope, it was possible to simultaneously obtain two dark field images at different collection angles, Figure 4.16. These images were acquired at inner collection angles of 26 mrads, Figure 4.16a, and 80 mrads, Figure 4.16b, from an $\omega$ containing region of the sample. The box profiles, Figures 4.16c & d, show the collapsing planes have a greater intensity than the non-collapsing planes in the LAADF condition, whilst the opposite is true in the HAADF image. These experimental observations are in good agreement with the multi-slice simulations shown in Figure 4.15, albeit that the magnitude of the intensity variation is less than that predicted. This difference is likely to be related to the number of perturbated planes within the sampled atom columns, and within those planes the magnitude of the atomic displacements. Nevertheless, the change in the position of the more intense columns at different collection angles is clearly visible. The consistency between the predicted and observed ADF images under the different microscope conditions and the absence of corresponding compositional variations in the EELS data indicate that the tri-layered structure may be attributed to the imaging conditions rather than compositional effects.
4.4 On the possibility of local structure in athermal $\omega$

Fig. 4.16 Images of a region containing the $\omega$ phase acquired simultaneously under a) LAADF and b) HAADF conditions, and c) & d) intensity profiles corresponding to the demarked regions within a) & b).

4.4.2 Discussion

In this section, the nature of the tri-layered structure associated with the $\omega$ phase was studied using high-resolution ADF imaging and EELS in Ti-15Mo (wt.%). Under HAADF conditions a tri-layer periodicity was observed in material quenched from the $\beta$ phase field, which appeared to be associated with the presence of the $\omega$ phase. The collapsing planes had a lower intensity than the non-collapsing planes. Whilst this may be attributed to atomic number contrast and, therefore, that the Mo atoms had a site preference within the $\omega$ phase, EELS data did not corroborate this interpretation. As a result, the origin of the intensity variation does not appear to be compositionally based. Instead, it is suggested that the tri-layer variation occurs as a result of scattering from atoms displaced from the ideal $\beta$ structure as part of the $\omega$ phase transformation. Multi-slice ADF simulations indicated that the $\omega$ structure could give rise to such periodicity, but that at smaller inner collection angles the variation in intensity between collapsing and non-collapsing planes should change. Simultaneous collection of ADF images at low and high angles confirmed this change, leading to the conclusion that the tri-layered intensity variations observed in HAADF images of Ti-15Mo (wt.%) are structurally driven, and an artefact of the microscope conditions, rather than being related to a compositional site preference.
Interactions between the imaging electrons and the sample can be elastic and coherent, elastic and incoherent or inelastic and incoherent. The majority of electrons incident on both LAADF and HAADF detectors are scattered elastically [179], therefore, coherency must be a factor. Whilst a LAADF detector will predominately collect coherent information and HAADF incoherent, the subtle changes in coherency between atom columns may be enough to alter relative intensity. This is known as coherency breaking.

Figure 4.17 is a simulated diffraction pattern of a \( \beta \) matrix that contains one variant of the \( \omega \) phase. Overlaid onto Figure 4.17 are the ADF detectors. Whilst a STEM diffraction pattern would be convergent, this TEM simulated diffraction pattern more clearly shows the position of the detectors relative to the first order diffraction spots. As such, a 20 mrad LAADF detector includes coherent scattering from both \( \beta \) and \( \omega \) structures. This can explain why the \{111\}_\beta columns, which had collapsed towards the \( \omega \) structure, contained a greater intensity to that of the stationary planes. This is because the perturbation resulted in inclusion of the reflections at 1/3 and 2/3 <112>\( \beta \) positions, thereby increasing the integrated intensity.

![Fig. 4.17 TEM simulated diffraction pattern of a \( \beta \) matrix containing a single \( \omega \) variant. The ADF detectors are overlaid.](image)

HAADF imaging is dominated by incoherent scattering, especially at inner collection angles which are greater than three times the probe semi-convergent angle. Critically, high angle scattering is not intrinsically incoherent as the signal is only made incoherent due to thermal diffuse effects and detector geometry. Therefore, the collapsed \{111\}_\beta may be breaking the coherency by a different amount to the stationary planes. This is important because coherent intensity is greater than incoherent intensity. For example, Equations 4.1 and 4.2 show the expected intensity for coherent and incoherent scattering for 10 atoms within a column with the average atomic number \( Z \) [179]. As Figure 4.12, Figure 4.13 and Figure 4.14 showed \( Z \)
to be consistent, a coherent atom column would be 100 times more intense than an incoherent column. Therefore, if the collapsed $\{111\}_\beta$ were less coherent than the stationary planes they would be less intense.

$$I_{\text{coherent}} = |10 \times Z|^2$$

(4.1)

$$I_{\text{incoherent}} = 10 \times |Z|^2$$

(4.2)

Coherency breaking can be separated into transverse and longitudinal components [179]. The transverse component is associated with the scanning directions whilst the longitudinal component is along the atom columns. The transverse component could not explain the HAADF tri-layer intensity motif. If both the collapsing and non-collapsing atoms were simultaneously illuminated, coherent interactions between the different columns could alter image intensity. However, due to the rastering nature of a high resolution STEM, neighbouring atom columns were imaged at different times; therefore, the interactions are incoherent. In fact, it is well established that detector geometry breaks transverse coherency in ADF imaging [179].

Scattering between atoms in the same atom column can result in coherent intracolumn interference. Unlike transverse interference effects, coherent longitudinal interference only becomes weakly incoherent due to the STEM setup. Thermal diffuse scattering (TDS) can significantly affect intracolumn coherency. The dwell time during scanning means multiple electrons are scattered at differing thermal atom positions (Deby-Waller effects), resulting in incoherent longitudinal scattering. Specifically, the collapsing $\{111\}_\beta$ planes to the $\omega$ phase may increase the proportion of incoherent interference due to a larger positional discrepancy than the stationary planes, resulting in less intense atom columns. This longitudinal coherency breaking could explain the observed tri-layer periodicity.

The $\omega$ phase breaking intracolumn coherency is significant for understanding the nature of the $\omega$ phase. This is because the degree of collapse can change the proportion of coherent interference to incoherent interference. This was investigated in section 4.5 by observing intermediate inner collection angles.
4.5 On the nature of the $\omega$ tri-layer periodicity in rapidly cooled Ti-15 wt.%Mo

4.5.1 Results

Figure 4.18a is a raw and uncorrected image of Ti-15 wt.%Mo following rapid cooling from the $\beta$ phase field, viewed along [011]$_{\beta}$. Within this HAADF image, two structures were observed, labelled $\beta$ and $\omega$. When considering the [200]$_{\beta}$ in the $\beta$ region, no atom column distortions could be observed in the $<1\bar{1}1>_\beta$. However, within the region labelled $\omega$ there were distortions towards the ideal $\omega$ structure but the precise extent of atom column collapse was difficult to determine. The reduced Fourier transform of Figure 4.18a, which is analogous to a conventional diffraction pattern, contains signal related to the $\beta$, circled, as well as unmarked frequencies at 1/3 and 2/3 $<2\bar{1}1>_\beta$. These unmarked reflections correspond to two possible variants of $\omega$, one of which is highlighted between the two parallel white lines in Figure 4.18a. Notably, the unmarked $\omega$ frequencies in Figure 4.18b are slightly distorted in the $<2\bar{1}1>_\beta$, which suggested a variation in the extent of collapse between the distorted columns. Figure 4.18c, which is an average background subtraction filter (ABSF) version of Figure 4.18a, exhibits less probe instability and emphasises the extent of the collapse. However, from these HAADF images, it was impossible to unambiguously ascertain if the atom columns were distorted by different amounts due to incomplete collapse, or if the mixture of collapsed and non-collapsing atoms in a column just appeared partially collapsed.

![Fig. 4.18](image)

Fig. 4.18 a) A raw and uncorrected HAADF image taken along [011]$_{\beta}$ of Ti-15Mo (wt.%) material that was quenched from the $\beta$ phase field. The $\beta$ and $\omega$ phases are labelled and the intensity box profile along [200]$_{\beta}$ is overlaid, b) The reduced fast Fourier transform of part a with the $\beta$ reflections circled, c) The same region as in part a but with a post processing ABSF applied.
4.5 On the nature of the \( \omega \) tri-layer periodicity in rapidly cooled Ti-15 wt.%Mo

The intensities of the atom columns within the white boxes in Figures 4.18a and c along \([200]_\beta\) are shown in each subfigure. In both cases, the intensity variation between atom columns in the \( \beta \) region contains no discernible periodic pattern. In contrast, within the \( \omega \) region, a periodic atom column intensity variation exists. The variation comprises an atom column with a higher intensity followed by two consecutive atom columns with lower intensity when considered along \([200]_\beta\). This tri-layer periodicity was shown in the previous section to be the coupling of the electron beam with the \( \omega \) phase. Figure 4.19a-c contain the same row of atom columns but imaged using inner collection angles of 39.0, 62.6 and 79.6 mrad respectively. These atom columns, which have had an ABSF applied, were taken from a region containing \( \omega \) as can be seen from \(<1\bar{1}1>_\beta\> distortions. For each microscope condition in Figure 4.19, the intensity profile along \([200]_\beta\) is also shown. In Figures 4.19a and b, the distorted atom columns, positions 2, 3, 5 and 6, have greater intensity than the non-collapsing atom columns, positions 1, 4 and 7. Figure 4.19c shows a different tri-layer periodicity to Figures 3a and b, with the non-collapsing atom columns at positions 1, 4 and 7 exhibiting greater intensity than the distorted atom columns at positions 2, 3, 5 and 6. A plot of the average intensity of the collapsing and non-collapsing atom columns as a function of inner collection angle is presented in Figure 4.19d. Linear extrapolation between the data points suggests that the tri-layer periodicity switches at approximately 75 mrad.

Previous research has shown that the tri-layer periodicity arises as a result of having an \( \omega \) precipitate in a \( \beta \) matrix [105, 106]. However, it was unclear if the \( \omega \) phase alone was the cause of the intensity variation, or if the tri-layer periodicity was related to the presence of the two phases in the atom columns. It has been experimentally shown that athermal \( \omega \) will form even under ultra-fast quench rates [30]. Therefore, simulations are required to determine how the individual phases interact with the electron beam. Multi-slice simulated ADF images from the \( \beta \), and ideal \( \omega \) phases, are shown in Figures 4.20a-c and d-f respectively. In each case, the structures were split into 52 layers along \([011]_\beta\), as described in section 4.2.3, with the beam direction shown by the arrow. The layer structures are shown schematically on the right of Figure 4.20, with the white layers representing the perfect \( \beta \) structure and black layers representing the ideal \( \omega \) structure. In these simulations, layers of the perfect \( \beta \) and ideal \( \omega \) structures were simulated with the same experimental conditions used for the collection of the images shown in Figure 4.19. For each simulated condition, atom columns along \([200]_\beta\) are shown, with their corresponding box profiles for the first 7 atom columns. Figures 4.20a-c do not exhibit tri-layer periodic intensity variations. The simulation in Figure 4.20c is in agreement with previously work [105], although that study did not extend to consider other inner collection angles. Similarly, the multi-slice simulations of
Fig. 4.19 a-c) ABSF ADF rows of the same (200)\(\beta\) but imaged using inner collection angles of 39.0, 62.6 and 79.6 mrad. The box profiles of pixel intensity are plotted above the atom columns for each case, d) a plot of relative intensity between the collapsing atom columns (i.e. those at positions 2, 3, 5 & 6) and the non-collapsing (at positions 1, 4 & 7) as a function of inner collection angle. Markers represent the mean and the error bars the standard deviation.
the ideal $\omega$ phase, shown in Figures 4.20d-f, exhibit no tri-layer periodicities between the atom columns for the different inner collection angles considered. The lack of any tri-layer intensity variations in these simulations demonstrates that imaging of the $\omega$ structure alone should not give rise to the observed periodicity.

Fig. 4.20 Multi-slice ADF simulations using only Ti atoms along $[01\bar{1}]_\beta$ of the perfect $\beta$ structure (a-c) and perfect $\omega$ structure (d-f) in which the inner collection angles 40, 60 and 80 mrad have been simulated. The schematic illustration shows the 52 layers involved with white representing the perfect $\beta$ structure and black the ideal $\omega$ structure.

Multi-slice simulated ADF images of two-phase mixtures of the $\beta$ and ideal $\omega$ phases are shown in Figure 4.21. Three distributions of the ideal $\omega$ precipitate within the $\beta$ were considered, as indicated by the slice schematic illustrations along $[01\bar{1}]_\beta$ shown on the right hand side of the figure. In all cases, the atoms involved in forming the $\omega$ phase were located within columns 2, 3, 5 and 6. For each distribution of the $\beta$ and $\omega$ phases, the integrated exit wave for inner collection angles of 40, 60 and 80 mrad are shown.
The \( \beta \) quenched condition and the athermal \( \omega \) phase

Fig. 4.21 Multi-slice ADF simulations containing two-phase mixtures of the \( \beta \) and ideal \( \omega \) phases, using 40, 60 and 80 mrad inner collection angles. The three different distributions of \( \omega \) in the \( \beta \) (a-c), (d-f) and (g-i) are shown in the schematic illustrations and the box profiles are plotted along \([200]\)\( \beta \).
4.5 On the nature of the ω tri-layer periodicity in rapidly cooled Ti-15 wt.%Mo

The distribution of phases used to create Figures 4.21a-c contained a block of ideal ω on the exit surface, such that the ω phase was the last structure through which the simulated electron wave propagated. The simulated atom column images in Figure 4.21a exhibit the largest degree of apparent collapse of any of the simulated images shown in Figure 4.21. Whilst it has been previously reported that the ω precipitates need to be near the exit surface in order to observe collapse [100, 105], Figures 4.21a-c show that this collapse is also more readily imaged at medium inner collection angles.

Critically, all of the multi-slice simulated ADF images in Figure 4.21 exhibit a tri-layer intensity variation. This suggests that the observed periodicity is related to electron wave interactions that occur in the presence of both phases. Irrespective of the position of the ω layers within the simulated distribution, different intensities are observed between the atom columns that contain displaced atoms, i.e. positions 2, 3, 5 and 6, and those that do not contain atomic displacement, i.e. positions 1, 4 and 7.

For all three different distributions of ω simulated, the images predicted for a 40 mrad inner collection angle, Figures 4.21a, d and g, that the collapsing atom columns contain greater intensity than the non-collapsing atom columns. Conversely, for all of the 60 and 80 mrad inner collection angles, shown in Figures 4.21b & c, e & f, h & i, the collapsing atoms show lower intensity than the non-collapsing atom columns. Therefore, irrespective of the position of the ω phase in the distribution, a switch in the tri-layer periodicity is wrongly predicted to occur between inner collection angles of 40 and 60 mrad.

Whilst the multi-slice simulations in Figure 4.21 reproduced the switch in tri-layer periodicity that was observed experimentally, the range of inner collection angles over which this occurred did not agree. To address this disparity, an alternative approach to describing the ω phase in the multi-slice simulations was implemented. In this approach, the overall structure was described using a frozen phonon, where the extent of collapse could take any value between the perfect β and ideal ω structures, based on Weibull statistics.

The multi-slice simulated ADF images created using the frozen phonon approach are presented in Figure 4.22. The degree of collapse present in each layer is indicated by the grey scale in the schematic to the right of the figure. For each layer there are two grey scale values, as each layer contains two collapsing atoms and the extent of collapse between distorted atom columns may be different [6].
The $\beta$ quenched condition and the athermal $\omega$ phase

Fig. 4.22 Multi-slice simulations along [011]$\beta$ for the inner collection angles of a) 40 mrad, b) 60 mrad and c) 80 mrad. Each simulation contains the same frozen phonon description of the $\beta$ and $\omega$ structure and is illustrated using a grey scale on the schematic.

In Figures 4.22a and b, the collapsing atom columns have greater intensity than the non-collapsing atom columns whereas Figure 4.22c shows that the non-collapsing atom columns have the greater intensity. This showed that the switch in tri-layer periodicity occurred between inner collection angles of 60 and 80 mrad, in agreement with the experimental results presented in Figure 4.19.

4.5.2 Discussion

Despite the effectiveness of multi-slice simulations in predicting the tri-layer periodicity, it is impossible to ascertain the extent of {111}$\beta$ collapse in an atom column using only HAADF modelling. This limitation exists as any level of collapse within the atom columns will result in the appearance of tri-layer periodicity [105]. However, results from section 4.4 suggested that the tri-layer periodicity switches when imaged under LAADF conditions. The LAADF tri-layer periodicity is the reverse of the HAADF tri-layer periodicity, with the collapsing {111}$\beta$ exhibiting a greater intensity than the non-collapsing planes. This observation has also been reproduced using multi-slice simulations. The switch in relative intensity between the two tri-layer periodicities emphasises the strong coupling between the propagating electron wave and the $\omega$ structure, which may help determine the extent of atom column collapse.
4.5 On the nature of the $\omega$ tri-layer periodicity in rapidly cooled Ti-15 wt.%Mo

Here, in agreement with previous work, the tri-layer periodicity seen in HAADF images of metastable $\beta$ Ti alloys has been shown to be correlated to the presence of the $\omega$ phase [105, 106]. This work has used multi-slice simulations of monolithic blocks of the $\beta$ and $\omega$ phases, as well as two-phase mixtures to show that the tri-layer periodicity is only apparent when there is a variation of atomic positions down an atom column, Figures 4.20, 4.21 and 4.22. This means that the material labelled $\omega$ in Figure 4.18 contains both the $\beta$ and $\omega$ phases and not simply the $\omega$ phase. However, modelling different descriptions of the $\omega$ phase using only HAADF conditions cannot be used to unambiguously identify the nature of the $\omega$ structure. This is because a precipitate of ideal $\omega$ in perfect $\beta$, as shown in Figure 4.21, and a frozen phonon description of $\beta$ and $\omega$, as shown in Figure 4.22, both displayed the tri-layer periodicity.

In this section, it has been shown experimentally that the relative intensity between the collapsing and non-collapsing atom columns changes with inner collection angle, Figure 4.19. At the lowest inner collection angle of 40 mrad, shown in Figure 4.19a, the collapsing atom columns exhibited greater intensity than the non-collapsing atom columns. This tri-layer periodicity was consistent with that reported in the Section 4.4 at 20 mrad. Whilst that study showed the two different tri-layer periodicities using simultaneous HAADF and LAADF imaging, the present work has also used the intermediate medium angle annular dark field (MAADF) imaging to determine the inner collection angle at which the tri-layer periodicities switch. In Figure 4.19d, the experimentally determined switch of relative intensity was found to occur at approximately 75 mrad.

The ADF images simulated using layers of ideal $\omega$ interspersed with perfect $\beta$, indicated that the switch in tri-layer periodicity occurred between inner collection angles of 40 and 60 mrad, as shown in Figure 4.21. The classic description of athermal $\omega$ phase is that of de Fontaine [164], which is a frozen soft phonon in $\langle 111 \rangle_\beta$. Using similar descriptions of the atomic displacements to those associated with this phonon mode [4, 6], further multi-slice simulations were performed, which predicted the switch in the tri-layer intensity periodicity for inner collection angles between 60 and 80 mrad. These results strongly suggest that the athermal $\omega$ present in Ti-15 wt.%Mo following water quenching from 785°C does not possess the ideal $\omega$ structure and that the extent of plane collapse is not complete.
4.6 Chapter conclusions

In this chapter, the nature of the tri-layered structure associated with the $\omega$ phase has been studied using high-resolution ADF imaging and EELS in Ti-15 wt.%Mo. Under HAADF conditions a tri-layer periodicity was observed in material quenched from the $\beta$ phase field, which appeared to be associated with the presence of the $\omega$ phase. The collapsing planes had a lower intensity than the non-collapsing planes. Whilst this may be attributed to atomic number contrast and, therefore, the Mo atoms having a site preference within the $\omega$ phase, EELS data did not corroborate this interpretation. As a result, the origin of the intensity variation did not appear to be compositionally based.

Instead, it is suggested that the tri-layer variation occurs as a result of scattering from atoms displaced from the ideal $\beta$ structure as part of the $\omega$ phase transformation. Multi-slice ADF simulations indicated that the $\omega$ structure could give rise to such periodicity, but that at smaller inner collection angles the variation in intensity between collapsing and non-collapsing planes should change. Simultaneous collection of ADF images at low and high angles confirmed this change, leading to the conclusion that the tri-layered intensity variations observed in HAADF images of Ti-15 wt.%Mo are structurally driven, and due to differing amounts of longitudinal coherency breaking, rather than being related to a compositional site preference.

Furthermore, the relative intensities of the atom columns within the tri-layer periodicity were shown to switch when the inner collection angle changed from 40 to 80 mrad. Measuring the intensities over intermediate collection angles identified that the switch occurred at 75 mrad. Multi-slice calculations were used to simulate the experimental conditions. These calculations showed that the intensities of the atom columns only varied when both the $\beta$ and $\omega$ structures were present in the atom columns. Atom columns with different descriptions of the $\omega$ and $\beta$ structures were also investigated. Whilst the calculations that contained discrete layers of both phases correctly predicted the tri-layer periodicity at 40 and 80 mrad, atomic positions defined using a frozen phonon provided a closer correspondence to the experimental results. Therefore, the collapse of atom columns towards the $\omega$ phase was not considered complete in this sample. The evidence presented in this chapter supports the classical frozen phonon model of omega formation.
Chapter 5

Thin foil artefacts; a new phase in Ti-15 wt.%Mo

5.1 Introduction

Generally, there is a need to develop a better understanding of the transformation sequences that can occur in metastable β Ti alloys during low temperature heat treatments, particularly with respect to transient transformations from the quenched condition [7, 75]. This is because the transient transformations could offer a potential alternative route for microstructural control.

Several studies have looked at the microstructural evolution of different metastable β alloys during low temperature heat treatments [2, 12, 41, 50, 66, 123, 125, 166]. In the course of these studies, additional non-equilibrium phases have been observed, some of which are thought to be transient [7, 78, 24, 73, 75, 82, 135, 180, 181]. In the Ti-Mo system transmission electron microscopy studies of relatively leanly stabilised alloys (with 6 and 8 wt.% Mo) indicated that the orthorhombic martensite, which was present following quenching, spinodally decomposed during low temperature heat treatments [24, 78]. This observation requires the existence of an orthorhombic phase with a composition intermediate to that of the equilibrium β and α phases. The occurrence of this phase is also supported by more recent X-ray diffraction data, where an orthorhombic structure was identified to form transiently prior to the equilibrium α phase in four different Mo containing commercial alloys: VT22 [58], Low Cost β [58], Ti-17 [135] and Ti-5Al-5Mo-5V-3Cr [135]. Based on the structure of this transient phase, it has previously been identified as the α" martensite [58, 135]. However, several factors brought this conclusion into doubt; the orthorhombic
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phase observed was formed during heat treatment, was compositionally distinct from its parent phase and no $\alpha''$ was identified following quenching from the $\beta$ phase field [7]. As a result, further studies were conducted on the orthorhombic phase in Ti-5Al-5Mo-5V-3Cr using high resolution (HR) electron microscopy. These results have indicated that the orthorhombic phase is, in fact, ordered and has a significantly larger unit cell than initially reported [73]. Critically, these studies highlighted the importance of comparing the quench microstructure to the heat treated condition and utilising multiple phase and spectroscopy techniques. Without which, the transient phases cannot be fully characterised and understood.

One suggestion is that the metastable $\beta$ titanium alloys could contain artefacts which are not representative of the bulk [79–84]. Instead, the transient phases may be attributed to the preparation of the samples. In this chapter, two artefacts are observed, both of which are the direct consequence of thin material. The first artefact is a thinning induced transformation, which perturbed the electron transparent regions. The second observation was the formation of a B2 structured phase during both in situ and ex situ thermal exposures at 300°C of pre-thinned material.

5.2 Methods

5.2.1 Thin foil preparation

Ti-15 wt.%Mo material in the $\beta$ quenched condition was thinned to electron transparency using twin jet electropolishing and focused ion beam (FIB) milling methods. The electropolishing method was the same as in Chapter 3 and Chapter 4 and involved a 8% HClO$_4$ solution in CH$_3$OH at -35°C and an applied voltage of 18 V.

The conventional method of FIB foil extraction from bulk material onto a copper grid followed by further thinning was not found to be successful. Therefore, an alternative method was employed. One foil of material was first thinned to 5 $\mu$m thickness by the electropolishing method and then further milled within a FEI Helios Nanolab FIB. Two trenches were milled completely through the foil thickness using Ga ions, leaving a 500 nm strip of material between the two trenches. The strip of material was then made into a cantilever by detaching one end. The through thickness rectangular cantilever was tilted and milled thinner in 100 nm increments taking side-on and top-down images after each milling step. At a critical thickness, foil distortion was found to occur. Due to the large attachment area of the cantilever,
the thin material was not lost. This thin foil was placed directly into a TEM without further milling of the foil. This was to ensure that the material was not subjected to any further forces.

### 5.2.2 Optical microscopy

Images of the foils were taken using an optical microscope with a calibrated scale bar. The images were taken under polarised light to enhance the foil features.

### 5.2.3 Electron microscopy and spectroscopy

Bright field (BF) images, dark field (DF) images and selected area diffraction pattern (SADP) were obtained using conventional transmission electron microscopy in the JEOL 200CX and a FEI Tecnai Osiris transmission electron microscopes (TEMs) both operated at 200 kV. Within the microscopes, the foils were tilted until thin electron transparent regions were aligned along low index zones.

Chemical information was obtained via energy dispersive X-ray (EDX) spectroscopy and electron energy loss spectroscopy (EELS) in the FEI Tecnai Osiris operated in scanning transmission electron microscope (STEM) mode using an FEI Super-X system and a Gatan Enfinium ER 977 spectrometer respectively.

EDX chemical maps were produced by quantifying the Ti-K and Mo-L X-ray signals at each pixel over an area of interest using the Gatan ESVISION software. During the quantification, a background was fitted followed by least-squares fitting of the Ti-K and Mo-L peaks to a model.

The Gatan Enfinium spectrometer contained dual EELS capability, where signal from two different energy ranges can be collected nearly simultaneously. For the EELS quantification, a collection semi-angle of 100 mrad was used and the integrated energy range evaluated for each edge of interest was 50 eV. Alloy composition was determined by k-factor analysis which used ionisation cross-sections taken from the standard Gatan database.

HR aberration corrected images, with sub-angstrom resolution, were acquired in an FEI Titan³ STEM, operated at 300 kV, using both high and low angle annular dark field detectors (HAADF and LAADF respectively). Atom columns were imaged down the low index
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$\langle 110 \rangle_\beta$ and $\langle 100 \rangle_\beta$ zones. The inner collection angle used to acquire the HAADF images was 80 mrad, whilst a 25 mrad angle was used to acquire the LAADF images.

### 5.2.4 Atomic force microscopy

An atomic force microscope (AFM) was used to measure the out of plane displacement of material around an electro-polished holes. The AFM was operated by Dr R.A. Oliver in a contact mode and surface height was established by the differential of the feedback signal. 3-dimensional reconstruction of the surface was performed using WSxM 5.0 AFM software.

### 5.2.5 Neutron diffraction

A 3 cm long, 8 mm diameter sample was cut from the material heat treated for 1 hour at 800°C. Phase analysis of this sample was investigated using data obtained from a neutron diffraction experiment performed by Dr M. Tucker using the neutron spallation source at ISIS, Harwell on the Polaris beam line.

The sample was contained in a vanadium can at room temperature and illuminated using a 5 x 5 mm neutron beam. The scattered neutrons were collected by banks of surrounding detectors at different angles which record the time of flight (TOF). After one hour, enough neutrons were scattered by the sample to contain a diffraction pattern with adequate statistics over a wide angular range.

The sample was then cooled to -263°C and left to stabilise for an hour. A second neutron diffraction measurement was performed with all other conditions kept constant, which allowed the material diffraction pattern to be directly compared between the two temperatures.

### 5.2.6 Differential scanning calorimetry

A cryogenic differential scanning calorimetry (DSC) was used to investigate phase transformations below room temperature. A 4 mm diameter disc of the quenched material was placed in a platinum, Pt, pan next to an empty reference pan. The machine baseline was calibrated to -115°C. From the initial $\beta$ quenched condition, the sample was cooled from room temperature to -150°C using liquid nitrogen at a rate of 10°C/min. The sample was
then returned to room temperature at the same rate. During cooling and heating, the relative heat flow required to change the temperature was measured.

5.2.7 Further heat treatments

From the section of material heat treated at 800°C, four 0.4 mm thick slices were cut perpendicular to the major axis using a diamond impregnated sectioning wheel. A 3 mm diameter disc was subsequently removed from each slice through spark erosion. Three of these discs, A, C and D, were immediately thinned to electron transparency. Disc B was left at its original thickness of 0.4 mm until after further heat treatment.

Disc A was left in the as-quenched condition, to provide a direct reference starting microstructure for all other samples from the same initial quench condition. Disc B was further heat treated in the un-thinned condition for 1 hour at 300°C in a Linkam TS1500V stage under flowing argon, before being thinned to electron transparency as described above. Disc C was studied *in situ*, during a heat treatment at 300°C, using a JEOL 200CX TEM operated at 200 kV and a single tilt heating stage. Whilst Disc D, which was pre-thinned, was subjected to an identical *ex situ* heat treatment to that of Disc B.
5.3 Thin foil features; quench condition

5.3.1 Results

The lath-like features

Figure 5.1 is an optical image of an electropolished hole made in material heat treated at 785°C for 1 hour followed by water quenching. Due to the preferential removal of material at grain boundaries, the electropolishing revealed some microstructural information in regions surrounding the foil holes. The microstructure was found to consist of equiaxed grains approximately 75 µm in size. At regions far from the hole edge, the grains did not contain any further characteristics. However, the equiaxed grains close to the electropolished hole contained lath-like features that were not seen further from the hole. Therefore, the lath-like features found at the hole edge are not considered representative of the bulk of material. From appearance alone, these features were initially hypothesised to be α″ martensite or β twins.

Under an electron microscope, it was found that material close to the hole edge could also be described by the two different appearances found optically. The differences were found for all the electropolished foils that contained β quenched material. Figure 5.2 is an indication of the two typical features observed. Within some regions, the lath-like features were present, whilst other areas were devoid of these features. An annular dark field (ADF) STEM image which highlights these differences is shown in Figure 5.2a. Box A in Figure 5.2a is an area that contains the lath-like features, whilst box B does not. In both cases, contrast variations were observed. Within box A, the contrast variation was periodic, whilst within box B a mottled contrast was apparent over the small protrusion of material. The ADF-STEM detector used to take this image is sensitive to incoherent Z-dependent signal, therefore, the intensity variations present could be expected to be due to differences in material composition. However, EDX-STEM mapping of box A and B show no variation in the Ti-K and Mo-L intensities, Figure 5.2b-e. Therefore, the contrast variation in the ADF image, Figure 5.2a, was not related to local composition variations.

Diffraction patterns along <110>β were taken from the regions highlighted by boxes A and B in Figure 5.2 and are shown in Figure 5.3a & b. The two diffraction patterns appeared similar despite one being taken from the region containing lath-like features, box A, and the other taken from an area representative of the bulk, box B; i.e. no additional phase information was apparent between the two diffraction patterns. Both diffraction patterns contained the β phase.
5.3 Thin foil features; quench condition

Fig. 5.1 A low magnification optical image of a thin foil sample used in Chapter 4 close to the electropolished hole. Lath-like features not considered to be representative of the bulk can be seen at the hole edge.
Fig. 5.2 a) ADF STEM image with a region containing lath-like features highlighted by box A and a region without these features shown in box B, b-e) EDX STEM images of the regions contained in box A and B. b-c) Ti-K and Mo-L intensity from box A and d-e) Ti-K and Mo-L intensity from box B.
and the athermal $\omega$ phase consistent with $\beta$ quenched alloys. Importantly, no diffraction spots relating to $\beta$ twins or martensite were observed in the regions that contained these laths. Bright field imaging of the laths over large tilts showed them to persist, which is a feature consistent with a thickness variation rather than a phase dependence. However, tilting showed that dislocations could be observed within the laths, Figure 5.3c. These dislocations were not observed in the bulk areas which implied they were linked to the features and possibly a remnant from deformation or a phase transformation.

Fig. 5.3 a-b) SADPs along $<110>_{\beta}$ taken from the boxed regions in Figure 5.2 and c) bright field image at tilt to show dislocations within the laths.

Figure 5.4a is a magnified optical image taken from the same foil as in Figure 5.1, which was the 785°C $\beta$ quench condition. A region in Figure 5.4a was scanned using an AFM Figure 5.4b. Within Figure 5.4b, contrast corresponds to surface height which helped in the identification of the lath features. A 3D reconstruction of the height map is shown in Figure 5.4c and a subsection of Figure 5.4c is shown in Figure 5.4d. The AFM scans, particularly the 3D reconstructions, clearly demonstrated that the lath-like features observed in TEM images are related to surface topography. Specifically, the brighter regions in Figure 5.4b are shown in Figure 5.4c & d are one half of a tent-like surface morphology, similar to what might be expected from a martensite transformation with internal twinning [169].

**Thermal martensite**

Despite the presence of martensite-like topography, no corresponding phase information related to a martensite phase was observed in the diffraction patterns, Figure 5.3b. Speculatively, a reversible martensite transformation may result in topography with irreversible
Fig. 5.4 a) Magnified optical image of the foil, b) AFM image where contrast corresponds to surface height, c) 3D reconstruction of a, d) subsection of part c showing the tent-like surface morphology indicated by the box.
surface relief. This reversible transformation might have occurred during the low temperature electropolishing stage of TEM foil preparation. To ascertain a possible martensite transformation at a temperature below room temperature, $\beta$ quenched material was cooled to $-150^\circ$C and the heat flow was measured using DSC. The change in heat flow as a function of the temperature is shown in Figure 5.5. Any phase transformations within the scanned temperature range can cause a change in the heat flow gradient from the baseline change. However, no gradient change that could be associated with a transformation was found on cooling to the electropolishing temperature ($\sim -35^\circ$C). Interestingly, on cooling to approximately $-100^\circ$C, a significant change in gradient was observed. Critically, this value was close to that of the lowest calibrated baseline gradient at $-115^\circ$C. Therefore, any data at a temperature below this value may not correspond solely to the material and must be interpreted with caution.

Fig. 5.5 DSC curves of $\beta$ quenched material being cooled to $-150^\circ$C at a rate of $10^\circ$C/min and returned to room temperature (indicated with arrows). The dashed line indicates the lowest calibrated baseline gradient at $-115^\circ$C.

Although DSC is a commonly used technique to identify phase transformations, it is limited by the fact that it is an indirect technique. Diffraction techniques provide direct information
about the change in structures associated with phase changes. As such, an \textit{in situ} diffraction was performed to investigate the crystal structures present at room and cold temperatures. Neutron diffraction data collected at both room temperature and at cryogenic temperatures are shown in Figure 5.6. Sharp $\beta$ peaks were observed at room temperature along with diffuse athermal $\omega$ intensity. Importantly, the diffraction pattern at -263$^\circ$C was identical to the $\beta$ quenched room temperature scan and in both cases there was no evidence of the martensite phase, which would contain additional diffraction peaks. The absence of these peaks is significant because the thermal martensite transformation was believed to exist in Ti-15 wt.%Mo below room temperature due to its superelastic properties during deformation.

![Fig. 5.6 Room temperature (RT) and cryogenic (10K) diffraction data recorded on the Polaris beam line, ISIS](image)

**Thinning induced transformation**

Critically, it can be deduced that the formation of the lath-like features observed must be due to the thinning process rather than induced by a temperature change. In order to simulate foil thinning in a controlled way, a cantilever of as-quenched material was cut using FIB milling. A side-on and top-down view of the milled cantilever is shown by Figures 5.7a & b. The material was incrementally thinned and then imaged from the top and side. Figures
5.7c & d are from an intermediate thinning step which showed the thickness of the cantilever to be reduced by 200 nm compared to Figures 5.7a & b. Possibly due to miss-alignment or beam channelling, the tip of the cantilever lost more material than the base, forming a wedge shaped geometry. This was deemed acceptable as wedge shape geometry was also found at the hole edge when using electropolishing techniques. Even though low forces were involved in Ga milling, at 250 nm thickness, the material spontaneously and rapidly deformed. At this point, milling was stopped and the final side and top images were acquired, shown in Figures 5.7e & f. At the end of the cantilever, some material has separated and rotated. Additionally, the cantilever tip had bent and contained serrations along the top.

![Fig. 5.7 FIB thinning of β quenched material taking images incrementally from the side and top.](image)

This FIB foil thinning procedure was repeated both in as-quenched material and on electropolished foils in regions far from the electropolished hole edge. In all cases, the cantilever progressively thinned until a limiting thickness was reached and the foil deformed. With the exception of the one shown in Figure 5.7, the cantilevers were lost. By chance, the one cantilever which remained after thinning was within an electropolished disc and could be...
viewed using a TEM. A bright field image and diffraction pattern taken from the cantilever edge are shown in Figure 5.8. At the very edge of the cantilever, Figure 5.8a, the serrations were very rounded which could be due to preferential localised Ga ion milling. Mottled contrast associated with the athermal $\omega$ phase was observed towards the thicker (darker) region of the cantilever. Between the $\omega$ containing region and the smooth serrations, periodic lath-like features were seen. An attempt to identify the diffraction information of these features is shown in Figure 5.8b. Within the $<110>_\beta$, the as-quenched diffraction pattern was observed. Specifically, only the $\beta$ and athermal $\omega$ phases were seen to be present. This was consistent with the diffraction pattern from the electropolished edge, Figure 5.3b, despite the different thinning procedure used.

Fig. 5.8 TEM bright field and diffraction pattern observations of the cantilever imaged in Figure 5.7.
Twinning

To understand the thinning induced transformation, multiple $\beta$ quenched foils were investigated to locate an area where the features did not terminate at a grain boundary. This was important to ascertain the relation between the $\beta$ matrix and the features. Figure 5.9a is a bright field image along [011]$\beta$ that show the laths converging to a point within the thickness of the $\beta$ matrix; i.e. this area was flat and did not have any topography. A diffraction pattern from the entire area in Figure 5.9a is shown in Figure 5.9b. Similar to Figure 5.3 and Figure 5.7, only $\beta$ and athermal $\omega$ reflections were present. However, one variant of the $\omega$ phase, such as those along 1/3 and 2/3 [2 1 1], had a greater intensity than the corresponding variant along 1/3 and 2/3 [2 1 1]. The diffraction pattern taken from the encircled region marked A in Figure 5.9a is shown in Figure 5.9c and is subtly different to Figure 5.9b despite still only containing $\beta$ and athermal $\omega$ reflections. The difference is that Figure 5.9c contained athermal $\omega$ reflections that have similar intensity between the two $\omega$ variants.

A closer inspection of the lath tips, for example region B in Figure 5.9b, revealed finer features within the laths similar to those observed in Figure 5.4 c and d. A diffraction pattern from these fine features (region B in Figure 5.9a) is shown in Figure 5.9d. Although the additional diffraction spots are faint, $\{112\}<111>\beta$ twins were observed. The $\beta$ matrix ($\beta_m$) and $\beta$ twin ($\beta_t$) are overlaid in Figure 5.9d for reference. Without the faint additional maxima in Figure 5.9d, the SADP from the twinned region appears very similar to a $\beta$ diffraction pattern with a dominant $\omega$ variant, for example $\omega_1$. Significantly, the brighter diffraction spots are not due to variant selection, they are the result of double diffraction from the two $\beta$ crystal structures and are independent of the $\omega$ phase.

For clarity, Figure 5.10 illustrates how the major reflections within Figure 5.9d are constructed without the $\omega$ reflections included. Figure 5.10a and b are drawings of the $\beta$ reflections from the matrix and twin. Figure 5.10c is a schematic illustration that contains overlapping $\beta$ matrix and twin spots. In addition, double diffraction spots from only the $\beta$ phase are included, which are labelled ’d’. To form these double diffraction spots, a g-vector is required from each of the matrix and twin. This is why the double diffraction spots are not included in Figure 5.10a and b. Together, the twin and double diffraction spots in Figure 5.10c appear like the diffraction pattern in Figure 5.10d, which is a reproduction of Figure 5.9d. It is now possible to see how Figure 5.10c and d may be construed to contain two phases; $\beta$ and one variant of $\omega$, leading to the double diffraction spots, marked ’d’, being mislabelled as $\omega_1$. 

Fig. 5.9 a) TEM bright field image of the tip of the area containing lath-like features. This image shows the internal features of the laths. b) SADP of the whole region shown in part a. c) Diffraction pattern from the circled region marked A in part a. The matrix spots from the parent $\beta$ phase are indexed. The position of the two $\omega$ variants, $\omega_1$ and $\omega_2$, are also indicated. d) Diffraction pattern from the circled region marked B in part a. The $\beta$ matrix, $\beta$ twin and double diffraction spots are indicated.
Fig. 5.10 a) Schematic illustration of the \(\beta\) matrix. b) Schematic illustration of the \(\beta\) twin. c) Schematic illustration of the matrix and twin. Double diffraction from the \(\beta\) is also given by the black spots. This schematic illustration is similar to \(\beta + \omega_1\) only. d) The same image as in Figure 5.9d and which directly corresponds to part c. The unaccounted reflections in part d are due to the \(\omega\) precipitates in the twin.
The reason Figure 5.9d can not be described as $\beta + \omega_1$ is because at high contrast, faint maxima are observed within the SADP. These additional spots can not be accounted for by $\omega$ variant selection. Instead, these maxima are due to the $\omega$ variants from the twin. To show this, Figure 5.11 is the same as Figure 5.10 except that Figure 5.11a-c includes the two $\omega$ variants in both the matrix and twin. The combined twin and matrix diffraction pattern, Figure 5.11c, also includes the double diffraction spots. Critically, Figure 5.11d is a high contrast reproduction of Figure 5.11c to show all of the faint $\omega$ reflections. It can be seen that, Figure 5.11d directly corresponds to Figure 5.11c. Interestingly, the two $\omega$ variants contain similar intensities, therefore, no evidence was found for stress induced $\omega$ formation.

Fig. 5.11 a) Schematic illustration of the $\beta$ matrix with less intense $\omega$ reflections. b) Schematic illustration of the $\beta$ twin with less intense $\omega$ reflections. c) Schematic illustration of the matrix and twin which also includes the $\omega$ reflections from both the matrix and twin. Double diffraction from the $\beta$ is also given by the black spots. d) The same image as in Figure 5.9d but with enhanced contrast to see the faint $\omega$ reflections. Parts c & d directly correspond. There are no unaccounted reflections and no requirement for stress induced $\omega$. 
The diffraction pattern in Figure 5.12a is taken from the region only contained within Figure 5.12b. According to Figures 5.11 and Figure 5.10 the diffraction spot encircled in Figure 5.12a is a double diffraction spot, which means it would illuminate twinned regions rather than the \( \omega \) phase. The corresponding dark field image is shown in Figure 5.12c and it was found that both the matrix and twin remained illuminated, a consequence of double diffraction which requires two \( \beta \) structures. In addition, the spot highlighted the lath features rather than the fine athermal \( \omega \) phase. Therefore, the encircled diffraction spot is not stress induced \( \omega \), instead it is associated with the \( \beta \) twin and this agrees with the proposed schematic illustrations in Figures 5.11c and Figure 5.10c.

**Fig. 5.12** A series of TEM images to show that double diffraction may be mistaken for an increased proportion of \( \omega \) within twins or stress induced \( \omega \). a) A diffraction pattern from the bright field region shown in part b. c) A dark field image using the encircled spot in part a.

### 5.3.2 Discussion

It was shown in Chapter 4 that Ti-15 wt.%Mo in the \( \beta \) quenched condition retained the metastable \( \beta \) phase and also contained the non-equilibrium athermal \( \omega \) phase. Here, compositionally indistinct lath-like features were found in thin regions of material close to the hole edge and were shown to be an artefact of the thinning process in Ti-15 wt.%Mo. The appearance of these features is consistent with other reports of non-equilibrium foil features found in the Ti-Mo system [51, 80–83, 139, 182]. However, there is disagreement as to the nature of these artefacts, with have been attributed to orthorhombic phases, hydride formation and twinning.
Hydride formation was discounted as the features were found to form during thinning at a critical thickness. In addition, no diffraction spots corresponding to a titanium hydride were found, although it has been suggested that hydride formation could be reversible [82]. Nevertheless, interstitial hydrogen uptake during etching electropolishing and FIBing is known to occur in β titanium alloys such as Ti-15 wt.%Mo [80, 82, 183]. Therefore, interstitial hydrogen may have influenced the formation of these features. For example, dislocation pinning by hydrogen may lead to a matrix which is more prone to twinning or martensite formation than dislocation motion [80].

The shapes of the lath-like features were very similar to the appearance of martensite in β alloys. In addition to the shape, the fine features are also a signature of internal martensite twinning. Martensite can form in two ways within Ti-15 wt.%Mo; thermal induced and stress induced. Ti-15wt%Mo is thought to have the thermal martensite start temperature suppressed to below room temperature. It may be that there were thermal triggers for this transformation during the cold foil preparation, which reverted upon returning to room temperature. For example, during electropolishing, the foil was subjected to a small jet of electropolishing media at -35°C. At locations that were in contact with this jet, either at the hole or very close to the hole edge, the material might have been sufficiently cooled to intercept the thermal martensite formation temperature. Figure 5.13 is a schematic phase diagram in which the two alloy compositions indicated by the red lines have enough β stabilising elements to suppress the martensite start (M<sub>s</sub>) temperature to below room temperature. In the case of the more leanly stabilised alloy, the M<sub>s</sub> trajectory is crossed at cryogenic temperatures. On returning to room temperature, a reversible transformation back to the β phase can occur. Equally, within Figure 5.13, the more stabilised alloy will never form the martensite phase. In the case of the Ti-Mo binary, the position that Ti-15 wt.%Mo falls between these two lines is not known. Similarly, the precise trajectory of the M<sub>s</sub> line is disputed [23, 24, 80], which makes extrapolation to electropolishing temperatures difficult. However, no evidence for the thermal martensite was found, even at 10K, Figure 5.6. This is confirmation of a previous hypothesis that the M<sub>s</sub> trajectory becomes invariant of temperature at a critical composition [119]. The implications are profound, especially for understanding stressed induced martensite formation. In particular, superelasticity in β alloys is predicted to only occur when stressing alloys at temperatures close to the M<sub>s</sub> temperature [184], Ti-15 wt.%Mo is known to have a superelastic response at room temperature but this work found no correspondence to the thermal martensite.
Fig. 5.13 A schematic representation of the pseudo-binary equilibrium phase $\beta$ alloy phase diagram at cryogenic temperatures. The two red lines indicate two alloys that have suppressed the $M_s$ to below room temperature. One alloy intercepts the $M_s$ temperature whilst the other never intercepts the $M_s$ trajectory.

Martensite is a deformation product in Ti-15 wt.%Mo [143]. In the foil thinning step, even at low flow rates, the force of the twin jets during electropolishing on thin regions may be sufficient to deform the foil. Therefore, FIB milling was used as an alternative and gentler method for thinning samples. Importantly, the same lath-like features were found to appear once the foil was 250 nm thick. Therefore, the deformation is more likely to be from stress relief rather than the thinning method itself. Some residual stress is expected in material which has been thermo-mechanically processed followed by water quenching. However, the formation of the athermal $\omega$ is also known to impart significant stress into the matrix due to the slight lattice parameter difference across the coherent interfaces [5]. Therefore, it is possible that no thermal stress relaxation treatments are possible for the $\beta$ heat treated condition.

A stress induced martensitic transformation, which relieves residual stress on foil thinning is a distinct possibility. However, it is not known what the driving force may be for the reversion of the martensite back to the $\beta$ phase. In addition, the appearance of $\beta$ twins at locations where internal martensite twins would occur is unusual and does not fit with martensite theory [185]. One argument is that the reversion of the martensite back to the $\beta$ phase does not necessarily require the $\beta$ variant to be the same as the parent, although this is difficult to prove. The discovery of $\{112\}<111>$ $\beta$ twins is the key to identifying these features. The foil edge appeared buckled, indicating the presence of compressive stresses. Therefore, deformation by twinning is entirely reasonable, especially if some interstitial hydrogen is
restricting dislocation motion. Consequently, instead of viewing the laths as the product of a reversible martensite transformation, they could be solely described by \(\{112\}<111>\) \(\beta\) twins with a zig-zag morphology. With a moderate stacking fault energy, it is feasible that a \(\{112\}<111>\) \(\beta\) twin may dissociate into three \(1/6<111>\) partial dislocations. These dislocations travel along separate \(\{112\}\) \(\beta\) planes in a \(<111>\) \(\beta\) direction. Obstacles to this motion, such as the \(\omega\) phase inhibit these dislocations until they can cross-slip to alternate \(\{112\}\) \(\beta\) glide planes, leading to a zig-zag morphology and subsequent lath appearance [186].

It was found that both parent and twin contained two variants of \(\omega\) reflections and all of these had similar intensities to each other. Where these reflections overlapped, the resulting intensity was much larger than the summed intensity. Therefore, it was deduced that these diffraction spots were predominantly double diffraction from the matrix and \(\beta\) twin. An important outcome of this work is that it is easy to misidentify \(\beta\) twins as stress induced \(\omega\) plates. This is because \(\{112\}<111>\) \(\beta\) twining, in conjunction with double diffraction reflections, was shown to appear very similar to parent \(\beta\) containing a dominant \(\omega\) variant. Consequently, this may be a significant reason why the interplay between the \(\beta\), \(\omega\) and martensite is reported to be complex [88, 147–154, 187].
5.4 Ordering in Ti-15 wt.%Mo

5.4.1 Results

SADPs from the as-quenched material, Disc A, viewed down a number of \( \beta \) zone axes are shown in Figure 5.14. The patterns shown in Figure 5.14a & c, which corresponded to the \([110]_\beta\) and the \([\bar{1}13]_\beta\) zones respectively, are typical of those reported for a metastable \( \beta \) alloy following quenching from the \( \beta \) phase field. They contain strong \( \beta \) reflections and weak, diffuse reflections at the 1/3 and 2/3 <112>\( _\beta \) positions, consistent with the presence of the two different athermal \( \omega \) phase variants visible in these \( \beta \) planes [88]. The diffraction pattern acquired along the \([001]_\beta\), Figure 5.14d, exhibits no unique \( \omega \) reflections, as the orientation relationship between the two phases results in identical interplanar spacings when viewed along this direction [7, 92]. A conventional DF image, acquired using the four \( \omega \) reflections within the circle marked on Figure 5.14a, is shown in Figure 5.14b. As can be seen, imaging the athermal \( \omega \) regions in this manner is extremely difficult and does not produce clear information as to the morphology or size of the phase. However, all of the data shown in Figure 5.14 is consistent with recent high resolution studies on material in the same condition, which found no evidence of any other phase being present.

An \textit{ex situ} heat treatment, expected to form isothermal \( \omega \), was performed on Disc B, which was thinned after thermal exposure. SADPs from this sample acquired down the \([001]_\beta\) and \([011]_\beta\) are shown in Figure 5.15a & b respectively. In the \([001]_\beta\) SADP, Figure 5.15a, only reflections corresponding to the \( \beta \) phase are apparent, whereas the presence of the \( \omega \) phase is clearly visible in the SADP acquired along the \([011]_\beta\), Figure 5.15b, where there is strong intensity at 1/3 and 2/3 <112>\( _\beta \). In addition to these strong independent \( \omega \) reflections, weaker reflections were also observed at 1/3 and 2/3 <110>\( _\beta \) and <200>\( _\beta \), labelled in Figure 5.15 by the letter d. However, these reflections were not seen in the \([001]_\beta\) SADP, Figure 5.15a, despite both the <110>\( _\beta \) and <200>\( _\beta \) being contained within the \{001\}_\beta. This suggested that the weaker spots, observed in Figure 5.15b, were a result of double diffraction, which was confirmed through their disappearance when the sample was subjected to small tilts away from the zone axis. A DF image of the isothermal \( \omega \) precipitates, produced using the four reflections encircled in Figure 5.15b, is shown in Figure 5.15c. It can be seen that the precipitates are fine scale (< 10 nm) ellipsoids and homogeneously distributed within the parent \( \beta \) matrix, consistent with previous reports using both TEM [65, 69] and atom probe tomography [12, 46, 64, 67].
Fig. 5.14 Overview of SADP from Ti-15 Mo (wt.%) in the $\beta$ heat treated and quenched condition, which contains reflections consistent with the presence of both $\beta$ and athermal $\omega$ phases, acquired along a) [011]$_\beta$, b) [113]$_\beta$, c) [001]$_\beta$ and d) DF image acquired using the four $\omega$ reflections indicated in part a.
5.4 Ordering in Ti-15 wt.%Mo

Fig. 5.15 Ti-15Mo (wt.%) heat treated at 300°C for 1 hour followed by electropolishing to a thin section, a) SADP down the [001]$_\beta$, b) SADP down the [011]$_\beta$, and c) DF image of the isothermal $\omega$ precipitates generated using the encircled reflections in b. The intensity maxima demarked d in part b are a result of double diffraction.

To elucidate the transition of the $\omega$ phase from the athermal to the isothermal state, an *in situ* TEM heating experiment was performed. Disc C, which was already thinned to electron transparency, was heated to 300°C in a double tilt holder. Prior to heating, the sample was aligned to the [001]$_\beta$ zone axis and an SADP and corresponding BF image of the microstructure acquired, Figure 5.16a & b respectively. The same region of the sample was observed during heating and realigned to [001]$_\beta$ once the temperature had reached 300°C. An SADP and corresponding BF image were acquired after a 15 minute exposure at the target temperature and are shown in Figure 5.16c & d. The SADP along the [001]$_\beta$ following thermal exposure, Figure 5.16c, was markedly different to that acquired at room temperature, Figure 5.16a. The reflections visible at room temperature were circular, whereas the same reflection positions at elevated temperature were asymmetric with an outward skew away from the transmitted beam (i.e. smaller d-spacings). In addition, new reflections were observed at positions of approximately $1/2 <200>_{\beta}$, which do not correspond to either the $\beta$ or $\omega$ structures. Therefore, these reflections indicated the presence of a new phase. The corresponding BF image, shown in Figure 5.16d, also exhibited a significant change from the equivalent room temperature image, Figure 5.16b. Following 15 minutes at 300°C a regular array of fine scale features could be seen in the material, with an approximately square cross-section.

Care must be taken when considering TEM data obtained from an *in situ* heat treatment experiment as diffuse scattering increases and thermal drift reduces the quality of the image. In addition, it was not possible to obtain diffraction data from other zones, as the heating stage had limited tilting capabilities. To overcome these issues, Disc D, which had already
Fig. 5.16 Images of Ti-15 Mo (wt.%) prior to and following *in situ* heat treatment at 300°C in the TEM. a) SADP down the [001]_β prior to heating, b) corresponding BF image of the microstructure, c) SADP down the [001]_β following 15 minutes at 300°C and d) corresponding BF image of the microstructure.
been thinned to electron transparency, was heat-treated \textit{ex situ} under identical conditions to Disc B. SADPs from the [001]_β and [011]_β of Disc D are shown in Figure 5.17, along with a BF image of the microstructure. The additional reflections located at \( \sim 1/2 \ <200>_{\beta} \), which were seen in Figure 5.16c, were also observed in the material heat treated \textit{ex situ}, Figure 5.17a. Similar additional reflections were observed at the same locations in the [011]_β SADP of the \textit{ex situ} heat treated sample, Figure 5.17b, along with reflections at 1/3 and 2/3 \(<112>_{\beta}\) corresponding to the \(\omega\) phase. The presence of additional diffracted intensity at locations that are consistent with the forbidden reflections of a body centred cubic (BCC) lattice, suggested that the new phase was a primitive cubic structure with a unit cell similar in size to that of the parent \(\beta\) phase. Interestingly, although both the [001]_β and [011]_β SADPs showed a cube-cube orientation relationship existed between the two phases, the alignment of the square cross-sectioned features seen in Figure 5.17c indicated that the faces of these features were along \{110\}_β rather than along the \{100\}_β as would be expected from a conventional cube-cube relationship.

Based on the evidence from the SADPs it seems likely that the additional reflections corresponded to the B2 structure, but this intermetallic phase has not been reported in the Ti-Mo binary system. Crucially, the formation of this phase would nominally require a 1:1 ratio between Ti:Mo and, therefore, significant local compositional changes would have had to occur during the short thermal exposure. In order to investigate whether such changes had occurred, material aged \textit{ex situ}, Disc D, was studied in an STEM instrument equipped with both EDX and EELS detectors. An ADF image of the microstructure is shown in Figure 5.18a. Significant intensity variations can be seen within the material with approximately square features, similar to those observed from the same area under conventional BF TEM conditions, Figure 5.17c. When imaging in ADF mode, intensity variations are a result of both chemical and strain inhomogeneities within the sample. EDX generated elemental distribution maps, acquired from the area within the box drawn on Figure 5.18a, are shown in Figure 5.18b & c for Ti and Mo respectively. The distribution map for Ti, Figure 5.18b, indicated the presence of compositional variation within the material, which corresponded to the features observed in the ADF image, Figure 5.18a. The narrow channels of bright contrast within the ADF image are enriched in Ti and surround approximately square cross-section regions that have a lower Ti concentration. However, the inverse trend was not observed in the Mo distribution map, Figure 5.18c, which did not show any significant variations in signal above the noise.
Fig. 5.17 Pre-thinned Ti-15Mo (wt.%) following an *ex situ* heat treatment at 300°C for 1 hour. 

a) SADP down the [001]_β, b) SADP down the [011]_β and c) BF image of the microstructure viewed along the [001]_β.
Another method of studying compositional variation in a STEM is to use EELS. However, the large difference between the edge energies of Ti and Mo make single detector measurement challenging, except at low energies (e.g. 200 to 700 eV). Unfortunately, within this energy range, the Mo M4,5 edge has a delayed edge onset and low signal above background. In addition, the close proximity of this Mo edge to the C K edge makes the accurate determination of the peak area difficult, even using advanced analysis techniques. To overcome these issues, two independent EELS energy ranges were used to make near simultaneous measurements over different energy ranges. One range covered 200 to 700 eV, which encompassed the sharp Ti L2,3 edges, whilst the second, set between 2000 to 2700 eV, captured the Mo L2,3. One of the most significant advantages of an EELS measurement with a binary alloy is the ability to quantify the compositions without reference to an external standard. The ratio of the post edge areas can be directly related to composition through the use of cross section analysis [188]. This analysis approach also suppresses the influence of sample thickness variations.

An ADF image of Disc D is shown in Figure 5.19a, corresponding to the area from which EELS data was acquired. The resulting dataset was processed using k factor analysis and the compositional profile of the line drawn on Figure 5.19a is shown in Figure 5.19b. The error in the calculated composition, indicated by the error bar on the first data point, was taken as the standard deviation in the entire EELS dataset. The compositional profile, determined from both the Ti and Mo EELS data, showed variations across the microstructural features well in excess of the error. The darker contrast square features in the ADF image, Figure 5.19a, appeared to have an elevated Mo content, whilst the brighter contrast channels were Ti rich, in line with STEM-EDX data, Figure 5.18b. However, exact correspondence between the ADF image and the EELS dataset is unlikely given the effect of beam drift and drilling at
thin length scale.

Fig. 5.19 a) ADF image of Ti-15Mo (wt.%) following an *ex situ* heat treatment of 1 hour at 300°C and b) composition variation along the line shown in part a determined through cross section analysis of EELS data. The arrows indicate the data corresponding to a Mo-rich B2 region and a Mo lean matrix region respectively.

As mentioned previously, the contrast observed in ADF images is generated by both compositional variation and strain. In both Figure 5.18a and Figure 5.19a, the Ti rich channels appeared brighter in contrast than the Mo rich phase. This would suggest that the signal is being dominated by strain, as the inverse contrast would be expected from the elemental partitioning. To establish this observation more conclusively, high and low angle ADF images were acquired, in which the contrast variation is dominated by composition and strain respectively. Raw LAADF and HAADF images, acquired simultaneously down the [001]_β, are shown in Figure 5.20a and b. It is immediately obvious that greater contrast variation exists in the LAADF image than the HAADF image, in line with the other ADF images.
Higher magnification, contrast enhanced, images from both modes are shown in Figure 5.20c & d. Both images contain perpendicular features with inverse contrast between the two modes. The HAADF image, which is dominated by composition, shows darker contrast channels between brighter, square-like areas, suggesting Ti rich channels and Mo rich square regions, in agreement with the spectroscopy data. The corresponding features in the LAADF image, which is strain dominated, indicate that the channel regions contain more strain than the new phase.

![Fig. 5.20 a & c) LAADF and b & d) HAADF images of the microstructure of Ti-15 Mo (wt.%) following an ex situ heat treatment of 1 hour at 300°C. Lower magnification images are shown in a & b. Higher magnification images are shown in c & d.](image)

Figure 5.21a is a raw high resolution HAADF image of Disc D along the [001]_β and the corresponding frequency map is shown in Figure 5.21b. Despite the contrast variations in the raw HAADF image being relatively faint, the fast Fourier transform (FFT) of the atom columns provides evidence of the B2 phase similar to the conventional SADPs presented.
Thin foil artefacts; a new phase in Ti-15 wt.% Mo

Fig. 5.21 a) Raw HAADF image acquired down the [001]_β from Ti-15 Mo (wt.%) following an ex situ heat treatment of 1 hour at 300°C, b) reduced FFT of part a, and c) intensity profiles taken from the corresponding boxes in part b. The arrows in c highlight the presence of the additional B2 phase reflections.

in Figure 5.17a. Whilst the eye is unable to distinguish the extra frequencies within Figure 5.21b, the additional maxima become clear when plotting the intensities within the two boxes as a function of position, Figure 5.21c. Within profile 1, which corresponds to a [200]_β, extra intensity is observed approximately half way between the central point and the {200}_β. In addition, the {200}_β frequencies appear to be separating into two distinct maxima. Similarly, this effect was also observed within profile 2, where the {110}_β peak had clearly split into two components, which are symmetric around the central point. These observations are also consistent with the asymmetry of the SADP reflections in Figure 5.16c. Thus, within the HAADF image both the β and B2 phases are present. Comparing the d-spacing of the {002} peaks with that of the {001} B2 indicated that the B2 phase had a slightly smaller lattice parameter than the β phase.

To examine the relationship and interface between these two phases in more detail, annular dark field images of the same region but at different magnifications were considered. As an orientation, Figure 5.22a presents a relatively low magnification LAADF image of the studied area viewed down a <100>β zone axis. The bright contrast strained channels, which were presented in Figure 5.20a, are clearly visible and are aligned with the <110>β. The material within region b was studied at higher magnification and the corresponding frequency map is shown in Figure 5.22b, which is essentially identical to that presented in Figure 5.21b. By selecting only the frequencies that correspond to the atom periodicities of the two crystal structures, a Fourier filtered image can be produced that suppresses background noise. The mask used in the present work is overlain on Figure 5.22b and was used to filter
an atomic resolution HAADF image acquired from region c, Figure 5.22c. The individual atom columns are clearly visible within the image and variations in their intensity, and therefore average atomic number, can be observed. To show this variation more clearly, the intensity of the entire row of atoms within the black box is plotted in Figure 5.22d. Moving from left to right, the atom column intensity changes from approximately even to showing a periodic brighter to darker variation. This change in intensity marks the boundary between the solid solution \( \beta \) phase and the ordered B2 structure, as shown by the schematic unit cells in Figure 5.22c. Interestingly, it is clear that the interface plane between the two phases is \( \{100\}_\beta \), which corresponds to the expected cube-cube orientation relationship between the \( \beta \) matrix and B2 precipitates, and not the \( <110>\beta \) alignment of the channels.
Fig. 5.22 LAADF image of the regions studied, showing the bright contrast strained channels, b) reduced fast Fourier frequency map from region b including the frequencies selected (within circles) to produce subfigure c, c) Fourier filtered HAADF image from region c and d) intensity profile of the atomic columns within the box shown in part c.
5.4 Ordering in Ti-15 wt.%Mo

5.4.2 Discussion

The elements that stabilise the $\beta$ phase are commonly separated into two categories based upon their binary phase diagrams. Elements such as Mo, Nb, Ta and V, which form continuous BCC solid solutions with Ti, are referred to as isomorphous additions, whilst elements such as Fe, Co and Ni, which form intermetallics with Ti, are known as eutectoid formers [29]. The intermetallic phase in these eutectoid systems is often a B2 structured phase but its formation in binary isomorphous element alloys has not been reported previously. Thus, the evidence presented in Figures 5.16 to 5.22, all of which indicates the presence of a B2 structured phase, is surprising.

Within the Ti-Mo binary system, several other phases are known to form, including the equilibrium $\alpha$ phase and two martensite phases, $\alpha'$ and $\alpha''$. However, all of these phases have lower symmetry crystal structures and markedly different lattices parameters, which are inconsistent with the data presented. For the same reason, the additional reflections seen in the SADPs from Discs C and D, Figure 5.16 and Figure 5.17, cannot correspond to the $\omega$ phase, as clearly shown in Figure 5.15a.

The Ti-Mo binary system has been reported to contain a miscibility gap, which suggests that alloys of a certain concentration would undergo a phase separation [6, 116, 119]. Recently, this concept has been adapted to develop the mixed-mode transformation mechanism in Ti-Mo alloy and used to explain the decomposition of the $\beta$ phase into $\beta + \omega$ [6]. However, this mechanism would not lead to the formation of a B2 phase and at no point during the present work has any evidence been found to suggest the co-existence of two BCC phases, required for a spinodal decomposition. In addition, if a phase separation was responsible for the occurrence of the B2 phase, it is unclear why this should not also have occurred in the bulk specimen, Disc B.

The fact that the B2 phase was only observed in the thin foils suggests that the material underwent a change in structure as a result of the electro-polishing step. It is not uncommon for thin foils to show different phase equilibria and behaviour to bulk material [80, 82, 83, 189]. During thinning, and despite the low temperature, it is possible the material may have taken up hydrogen, which has significant solubility in the $\beta$ phase. It has been suggested that this hydrogen could be retained following electro-polishing if a sufficiently thick oxide layer exists on the sample [82]. The presence of hydrogen within the material during thermal exposure would either stabilise the $\beta$ phase or, if present in significant concentration, could result in the precipitation of hydride phases [190]. If hydrides were assumed to form, then
they would be expected to exist as either the face centred cubic, $\delta$, or in a tetragonally distorted form, depending on the exact hydrogen concentration [82, 190, 191]. However, when considering typical lattice parameters for these phases in the Ti-Mo system, $\sim$4.431 Å for the $\delta$ phase and $\sim$3.186 and $\sim$4.107 Å for the tetragonal phase [191], there are no allowed reflections that have interplanar spacings consistent with the 1/2 $<200>_{\beta}$ positions observed in the present work. As a result, hydride formation cannot account for the observed features in the experimental diffraction patterns.

Hydrogen is a potent $\beta$ stabilising element and has significant solubility within the $\beta$ phase, up to $\sim$1.5 at.% [190] but it exhibits no appreciable solubility in Mo [192]. As a result, any uptake of H during electro-polishing could have altered the thermodynamics of the system prior to heat treatment. Given the immiscibility of H in Mo it is possible that the presence of H in the thinned samples could have promoted some form of $\beta$ phase separation, leading to the formation a B2 phase, that would not be observed in a bulk specimen. However, the assessment of local hydrogen concentration is extremely complicated and beyond the scope of the EDX and EELS techniques employed in this work. Thus, at present, the role of hydrogen in mediating the formation of the B2 phases is unestablished.

The production of a thin foil also reduces the local constraint on the specimen, which would have been previously imparted by the surrounding material. This alteration could also affect the local thermodynamics of the system, as the strain contribution to the Gibbs energy is lessened. Since the B2 phase was found to possess a smaller lattice parameter than the $\beta$ phase, Figure 5.21, its precipitation in the $\beta$ matrix would create a surrounding strain field, as shown in Figure 5.20. Without the presence of a free surface the magnitude of these strains within the $\beta$ phase could be higher and may inhibit the formation of the B2 phase. Thus, it is conceivable that the Gibbs energy of the B2 phase may only offer the lowest energy state in a thin foil. However, without further investigation, the relative contributions of these different effects cannot be established and so the precise reason why the B2 phase only appears to form in thin foils remains unclear.

Whilst, the results presented here are the first direct evidence of a B2 structure existing in the Ti-Mo system, similar microstructures comprising different phases have been reported before in Ti-Mo alloys with lower Mo concentrations. Cellular microstructures on the same length scale to those reported here, have been observed in Ti-(4-8) Mo (wt.%) alloys following thermal exposure at temperatures between 450 and 550°C [78]. These alloys were quenched from the $\beta$ phase field prior to thermal exposure but, due to the lower Mo content, these
alloys all underwent a $\beta$ to $\alpha''$ transformation. It was reported that the $\alpha''$ phase in these alloys contained very fine scale modulations, but no further information was provided. Upon thermal exposure, the modulations coarsened into a $\sim 5$ nm regular cubic array, similar to that shown in Figure 5.16, Figure 5.17 and Figure 5.19, before becoming the equilibrium $\alpha$ and $\beta$ phases. No additional reflections were apparent in the diffraction pattern presented and so the authors came to the conclusion that the orthorhombic martensite had undergone a spinodal decomposition. However, a detailed analysis of the cuboidal arrays shown in the TEM images was not presented, possibly since such an analysis may have been beyond the instrument’s capabilities at the time. Therefore, it is possible that the transient phase captured by Davis et al. [78] is the same B2 phase observed here. Even, if not the case, this early study highlights the possibility of transient phases during heat treatments in binary Ti-Mo alloys.

Outside of the Ti-Mo system, tweed microstructures containing a B2 structure have been observed in Ti-Al-Nb alloys [193]. In addition to the similar appearance of the tweed to the square-cross section features reported here, the same $<110>_{B2}$ directionality is observed in material that also contains the $\omega$ phase. It is thought that the tweed microstructures in these shape memory alloys are a precursor to the martensite transformation (possibly inhibited by the $\omega$ phase) and are caused by the softening of $<110>$ phonon modes [193]. In theory, material close to a martensite transformation could be triggered by a strain energy gradient analogous to the role of composition in traditional spinodal decomposition [194]. This strain spinodal, containing regions of high and low strain, might explain the nature of the tweed microstructures and the $<110>_{\beta}$ square cross sections shown here. Interestingly, it is argued that thin material, which includes effects from two surfaces, may be sufficient to place the free energy density as a function of strain close to a strain spinodal [29]. Therefore, it is possible that the B2 phase observed here could be the result of a complex interaction between $<110>$ phonon softening and thin foil effects during transient phase formation.
5.5 Chapter conclusions

The phase and microstructural evolution of Ti-15 wt.%Mo following water quenching and subsequent treatment between -283 and 300°C was characterised using a range of high resolution techniques. A thinning-induced transformation was found, which resulted in lath-like features around the foil edge within the electron transparent regions. These features were found not to be a thermal or stress induced martensite, but instead the features were \{112\}<111>β twins, which were difficult to identify due to double diffraction effects. The consequence of this double diffraction was the apparent occurrence of a dominant ω variant which may have been mistakenly identified in previous research.

A 0.4 mm thick disc was isothermally heat treated \textit{ex situ} at 300°C for one hour. Following this exposure, no discernible change in the microstructure had occurred but the diffraction spots corresponding to the ω phase had sharpened. This is thought to be consistent with the structural and chemical alterations associated with the transition of athermal ω to isothermal ω.

Similar 0.4 mm discs were thinned to electron transparency through twin jet electro-polishing before undergoing thermal exposures at 300°C, both \textit{in situ} and \textit{ex situ} of the electron microscope. In both samples, new additional reflections were observed in selected area diffraction patterns, consistent with a B2 structured phase. In addition, regular arrays of square cross section precipitates separated by thin channels became apparent in the electron images. The alignment of the diffraction patterns suggested that the two phases had a cube-cube orientation relationship. Compositional analysis using EDX and EELS indicated that the precipitates were enriched in Mo, whilst the surrounding channels were enriched in Ti. Low and high angle ADF imaging supported the compositional analysis and indicated that the channels contained an elevated level of strain. Analysis of high resolution images of the atom columns showed that the lattice parameter of the B2 phase was smaller than that of the β phase, rationalising the observed strain in the channels.

Whilst this is believed to be the first observation of the B2 phase in a Ti-Mo binary alloy, its formation is also thought to be a thin foil effect, as this phase was not observed in the bulk sample. The exact mechanism enabling the formation of the B2 phase in the thin foils is unknown, but is hypothesised to be due to hydrogen up-take, reduced constraint, or a combination of the two.
Chapter 6

The athermal \( \omega \) to isothermal \( \omega \) transformation in Ti-15 wt.%Mo

6.1 Introduction

There is evidence suggesting that the isothermal \( \omega \) phase provides a fine distribution of sites for heterogeneous nucleation of the \( \alpha \) phase [42, 48, 57, 66, 166]. However, in order to precipitate isothermal \( \omega \), \( \beta \) alloys first require rapid cooling from high temperatures otherwise equilibrium \( \alpha \) precipitation will dominate. Critically, it is known that a \( \beta \) quench will also yield the athermal \( \omega \) phase [22, 30]. Therefore, how the transformation between the athermal \( \omega \) phase and the isothermal \( \omega \) phase occurs poses an intriguing question [59].

Characterising a transition between the metastable phases in \( \beta \) alloys is not trivial due to the small size of the precipitates and the small atomic-level alterations involved. As a result, little is known about the transformation of the athermal \( \omega \) (\( \omega_{\text{ath}} \)) to the isothermal \( \omega \) (\( \omega_{\text{iso}} \)) phase. It has been established by modern atom probe tomography (APT) isosurface analysis that there is a compositional component in the formation of isothermal \( \omega \) [2, 5, 12, 39, 46, 66, 67]. On heating, \( \beta \) stabilising additions are rejected from the isothermal \( \omega \) phase, facilitating the growth of precipitates which are typically larger than athermal \( \omega \) but still smaller than \( \alpha \) precipitates [14]. However, small super-refined \( \alpha \) precipitates have been reported when heterogeneously nucleated on isothermal \( \omega \) [39, 42] and may be the driving force for rejection of stabilising elements. Similarly, the isothermal \( \omega \) composition has been speculated to be only the \( \beta \) lean portion of a \( \beta \) phase decomposition and not intrinsic to the metastable phase [2, 30]. Where isothermal \( \omega \) composition has been measured, the equilibrium composition is still debated (see [2, 5, 30] and Chapter 3). It is also known that the structure of isothermal \( \omega \)
is hexagonal [50]. Therefore, any incomplete collapse of the \{111\}_β in the athermal ω phase (either from a β frozen phonon [4] or block trigonal ω structure [105]) might shift to the ideal ω structure during isothermal ω phase formation before diffusion occurs [2]. This hypothesis may explain the change in diffuse ω diffraction intensity to sharp Bragg reflections [29]. Alternatively, this change may also be a size (growth of athermal [67] or isothermal ω [59]) or alternative volume fraction effect such as precipitation of more athermal ω [67].

Several in situ techniques have been used to measure and understand the athermal to isothermal ω transformation: resistivity measurements [54, 57–59, 71, 72, 156, 195–197], X-ray and neutron diffraction [41, 163, 195, 198–202], calorimetry [31, 57, 162, 200], and ultrasonic resonance [56]. In addition, many of these studies have been accompanied by electron microscopy examination. This body of research has led to several theories about the ω_{ath} → ω_{iso} transformation. In the simplest case, isothermal ω formation is a first order transformation [59] in which the athermal ω precipitates are nuclei or embryos of the isothermal ω phase [2, 48, 66, 139, 203]. There is also some evidence that this diffusional transformation might be second order due a continuous composition variation [2, 30]. However, no evidence could be found for this within Chapter 4. Similarly, the ω_{ath} → ω_{iso} transformation is sometimes described as a mixed mode displacive-diffusional transformation [2] as athermal ω does not have to exhibit the same structure as isothermal ω [204]. As the average athermal ω structure may vary with composition [7], if this were the case, it could be that the transformation would vary significantly between different metastable β titanium alloys [89].

Alternatively, it is worth considering that isothermal ω formation is not necessarily the result of an ω_{ath} → ω_{iso} transformation and could be formed straight from the β matrix, i.e. β → ω_{iso}. If this were the case, a reduction in athermal ω precipitates, β + ω_{ath} → β, may also have to occur [54, 59, 71]. This deduction was made from observing reversible resistivity and calorimetry responses, associated with athermal ω dissolution, at temperatures below which significant diffusion could occur i.e. the dissolution of athermal ω at these temperatures can only be a displacive transformation. Therefore, a structural change may precede the compositional change when forming isothermal ω from the quenched condition. However, the atomic structure and composition of material is not directly measured in resistivity and calorimetry studies, the technique is indirect and results should be interpreted with caution. This makes it difficult to establish a transformation pathway and questions the validity of the β + ω_{ath} → β → β + ω_{iso} pathway.
Changes in the crystal structure can be directly measured using diffraction techniques. This is done by considering the position and intensity of the Bragg peaks [205]. Direct diffraction based studies have been conducted specifically to measure the reversible $\beta + \omega_{\text{ath}} \rightarrow \beta$ aspect [29, 89, 198]. In these studies, the change in athermal $\omega$ diffraction intensity was measured between room and cryogenic temperatures, which prevented diffusion. Critically, the observed reversibility of this transformation at low temperatures was attributed to the change in diffuse scattering rather than the long range crystal structure [198], a conclusion also found in $\omega$ forming in the Zr-Nb binary [90]. However, the same may not necessarily be true in the 0-400°C range where diffusion is promoted rather than restricted.

In order to further clarify the pathway of the athermal to isothermal $\omega$ transformation, a technique is required which can directly observe the structural changes whilst at the same time distinguishing between long range Bragg changes and short range diffuse changes. A technique that can offer this type of analysis is called Total Scattering, where long range and short range information is considered concurrently [205]. The traditional use of total scattering was to identify the difference between average structure and local structure as a means to investigate disordered materials. For example, early investigations were conducted on liquid metals such as the study of the structure of mercury [206]. With the development of high quality diffraction tools, more recent studies have focused on quasicrystalline materials using synchrotron facilities [207–209]. Whilst total scattering was predominantly developed for quantifying order within disordered materials [210], the same analysis can be used to investigate the amount of disorder in crystalline materials [8, 211, 205]. Therefore, as the $\omega$ phase can be described as a perturbation of the $\beta$ structure, this technique may be a useful tool in understanding $\omega$ formation.

Here, the $\omega_{\text{ath}} \rightarrow \omega_{\text{iso}}$ in Ti-15 wt.%Mo has been studied using total scattering and complementary analyses. It was found that analysis of total scattering data using the pair distribution function (PDF) method required only a minimal number of assumptions in order to interpret the transformation. However, in practise, a combination direct and indirect techniques was shown to be the most beneficial for understanding this complex transformation.
6.2 Methods

6.2.1 Material and heat treatment

An 8 mm diameter bar of extruded Ti-15 wt.%Mo was heat treated for 1 hour at 800°C followed by water cooling. This process was identical to that in Chapter 3. 3 mm x 4 mm x 5 mm parallelepipeds of material were machined from the bar for resonant ultrasound spectroscopy (RUS) performed by S. Driver [212]. A 3 mm diameter disc with a 0.5 mm thickness was also electro-spark cut from the bar. This sample was used for differential scanning calorimetry (DSC).

The remaining material, weighing approximately 10g, was gas atomised by ATOMIZE GmbH into a powder. In the process of gas atomisation, this material from the homogenised bar was locally melted and dispersed using inert gas jets. The droplets solidified from the high temperature $\beta$ phase and since heat is lost rapidly, the powder was effectively quenched. The quench rate was not measured. The powder was stored in an argon environment to minimise oxygen uptake. However, the powder was sieved in air using a 32 $\mu$m mesh to reduce the average powder size and thereby maximise sampling statistics for X-ray diffraction analysis. It is possible that some contamination occurred at this stage. After sieving, the powder was filled into fused silica capillaries that had a 0.5 mm diameter and a 0.1 mm wall thickness. The filled capillaries were then individually placed in glass tubes and evacuated to remove oxygen. Alumina wool placed at the top of the capillaries prevented the loss of powder into the vacuum pump. After several argon purges, the glass capillaries were sealed in an inert atmosphere.

The powder samples were then heat treated as detailed in Table 6.1. Following thermal exposure for 100 hours, the powder filled capillaries were air cooled to prevent capillary breakage. However, as the capillaries were thin, the cooling rate was relatively fast. The samples heat treated for 100 hours at 200, 300, 400 and 500°C were used to collect Bragg data using transmission X-ray diffraction. The sample left at room temperature was used for a total scattering experiment which included in situ heat treatments.

High temperature heat treatments were also conducted but sintering and oxidation of the powder was significant. Post heat treatment examination of the sintered powder showed $\alpha$ formation, where the powder particles sintered together, despite being heated above the $\beta$ transus. Therefore, this data has been omitted. However, it was interesting to find that a higher local concentration of oxygen on the powder surfaces stabilised the $\alpha$ phase, similar
to $\alpha$-case formation which can be found when titanium is heat treated in air [29].

<table>
<thead>
<tr>
<th>Age Temperature (°C)</th>
<th>Age Time (Hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT</td>
<td>-</td>
</tr>
<tr>
<td>200</td>
<td>100</td>
</tr>
<tr>
<td>300</td>
<td>100</td>
</tr>
<tr>
<td>400</td>
<td>100</td>
</tr>
<tr>
<td>500</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 6.1 Details of the thermal treatments. After thermal treatment, the material was air cooled.

6.2.2 Differential scanning calorimetry

DSC was conducted on a piece of quenched Ti-15 wt.%Mo. The sample was heated at a rate of $10^\circ$Cs$^{-1}$ during which the change in heat flow was recorded and normalised against the initial heat flow. The material was heated to 450°C followed by cooling at the same rate to room temperature.

6.2.3 Resonant ultrasound spectroscopy

An *in situ* resonant ultrasound spectroscopy (RUS) experiment was performed by S. Driver on cuboids of Ti-15 wt.%Mo in the $\beta$ quenched condition. The cuboids were held between a drive alumina transducer arm and a pickup transducer arm within an inert environment furnace. One sample was was heated to 500°C in 5°C increments. A second sample was heated to 850°C in 5°C increments followed by cooling to room temperature at the same rate. At each temperature increment, the sample was scanned for one hour across a 100-1200 kHz frequency range using the drive transducer. Across this range, resonant frequencies of the sample were found by measuring the signal in the pickup transducer. The positions of these peaks were analysed by S. Driver to give an indication the modulus by means of a frequency$^2$ term using Equation 6.1.

$$k = (2\pi f_n)^2 m \tag{6.1}$$

Where $f_n$ is the natural frequency, $k$ is the stiffness and $m$ is the mass. Since there is no analytical solution for deducing the exact elastic modulus terms from the resonances, an indirect
least squares computation can be performed based on assumptions of the elastic modulus and weight coefficients. In this case, the precise measurements of the bulk modulus were not determined as a satisfactory fit could not be achieved. Therefore, the change in frequency term was only used to show the relative change in modulus between room and higher temperatures.

6.2.4 Transmission X-ray diffraction

Transmission X-ray Bragg scattering data were collected at the Diamond Light Source synchrotron facility on the I15 beam line. A brilliant 70 \( \mu \text{m}^2 \) X-ray beam with an energy of 75.5 keV was transmitted through rotating (720 r.p.m.) silica capillaries filled with < 32 \( \mu \text{m} \) powder. The transmitted X-rays, in the form of Debye-Scherrer cones were collected using a Perkin Elmer 2D detector which imaged the cones as rings around the tungsten central beam stop. Bragg scattering data was collected at room temperature for the heat treated powders described in Table 6.1. Due to the intensity of the X-rays, only a couple of seconds of data acquisition were required for each sample otherwise the detector saturated. In addition to the Ti-15 wt.%Mo powder, a CeO\(_2\) standard sample was run to ascertain instrumental parameters.

6.2.5 Total scattering

Total scattering data was collected on the same beam line as the transmission X-ray diffraction data but with the detector positioned only 110 mm from the sample. In addition to the rotating sample holder, a N\(_2\) gas blower was introduced to enable \textit{in situ} thermal treatments. Total Scattering experiments require and rely on collecting high quality data at a high scattering angular range, hence the position of the sample. Acquisition parameters were carefully selected to maximise X-ray exposure whilst minimising detector saturation over the acquisition period. The least detector ghosting (after image) was found to occur by taking a one minute dark field (DF) scan (X-ray shutter shut) of the detector to record detector noise followed by ten one minute bright field (BF) (X-ray shutter open) scans which record the transmitted X-rays. Each of the one minute scans were subsequently corrected by subtracting the DF values. Whilst some detector ghosting was apparent after ten minutes due to slightly inaccurate detector correction, this process prevented detector saturation.

Ten minutes of BF acquisition were taken of the empty instrument to account for air scattering effects. Within this condition, no capillary or sample was contained in the spinner. However, the capillary spinner and gas blower themselves were left in place as the position of these did
not change over the course of the experiments. It was important to take an image of the empty instrument since the samples were positioned close to the detector, which was approximately 0.5 m from the shutter. Therefore, X-ray air scattering, which was partly absorbed by the spinner and gas blower, caused a shadow onto the detector. This was subsequently removed by subtracting the empty instrument scans from the scans containing the sample. Similarly, an empty capillary was also imaged at each of the temperatures of interest. This is because the fused amorphous silica also weakly scatters the X-ray beam. Importantly, the silica was amorphous, which meant it did not cause Bragg scattering. However, the silicon (Si) and oxygen (O) atoms still contain local structure in amorphous SiO$_2$. By taking scans of empty capillaries, the impact of this local structure could also be removed from the total scattering data.

During the *in situ* experiment, powder was heated incrementally to each of the temperatures listed in Table 6.2. At each temperature step, the powder was held for 30 minutes in total. The first 10 minutes of each step were not recorded as time was given for the atmosphere around the capillary to reach the target temperature. X-ray data in the second 10 minute period showed the thermal stabilisation of the powder (shown by subsequent analysis of lattice parameter change to equilibrium values). The final 10 minute periods were used for total scattering analysis.

<table>
<thead>
<tr>
<th>Age Temperature (°C)</th>
<th>Time at temperature (minutes)</th>
<th>No. bright field scans</th>
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<tbody>
<tr>
<td>RT</td>
<td>11</td>
<td>10</td>
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<td>100</td>
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<tr>
<td>450</td>
<td>30</td>
<td>20</td>
</tr>
</tbody>
</table>

Table 6.2 Thermal treatments investigated within the *in situ* transmission X-ray diffraction experiment.
6.2.6 Bragg analysis

The 2D detector images were analysed using Dawn software [213]. Using data obtained from the certified CeO$_2$ standard, the central position of the Debye-Scherrer rings was determined by Dr L. Conner using the known CeO$_2$ lattice parameters. A detector mask was also constructed that prevented data from anomalous pixels and the beam stop being included in the ring integration. For each detector image acquired, the Debye-Scherrer rings were integrated over the full 360° azimuthal angle and saved as raw data in intensity versus 2θ format. Data that did not have 360° azimuthal coverage, a result of a square detector, were not used. This decision was taken to avoid extrapolation errors that may be introduced by including the edge information.

The raw data were converted into a format that can be analysed using the general structure analysis system (GSAS), a structure refinement software [214]. Within GSAS, the data file was imported along with the instrument parameter file. The data was fitted to $\omega$, $\beta$ and $\alpha$ structures imported from the National Chemical Database Service (located at www.cds.rsc.org). It was found that fitting was best performed between 2° and 12° 2θ due to high signal-to-noise ratio. The background was fitted using a shifted Chebyshev function with up to 20 terms. The large number of terms required to fully fit the background was due to the diffuse nature of the $\omega$ phase. In general, the best approach was to fit the peak shape and lattice parameters for the background data using a Le bail method [214]. After which, the fitted peak shape obtained was kept constant and the volume fraction obtained using the Rietveld method [214]. Further refinement was conducted by allowing the isotropic displacement parameter (U$_{iso}$) to vary. Finally, phase information, such as fractional coordinates and occupancies, were refined until convergence to the smallest least squares fit. Critically, at this stage, the correct constraints had to be imposed otherwise the fit tended to diverge.

6.2.7 Total scattering analysis

Total scattering analysis was conducted in Gudrun software [215] and the raw data transformed from $\theta$ into $Q$ (units Å$^{-1}$) using Equation 6.2.

$$Q = |Q| = \frac{4\pi \sin(\theta)}{\lambda}$$ (6.2)

The aim of this analysis was to transform reciprocal diffraction data into useful and intuitive real space information. The relationship between the reciprocal space information $Q$ and real
space information $R$ is shown by Equation 6.3.

$$\psi(Q) = \frac{1}{<b>} \sum_v b_v e^{iQ \cdot R_v}$$  \hspace{1cm} (6.3)$$

Where $\psi(Q)$ is the scattering amplitude, $b_v$ is the scattering amplitude of atom type $v$, $<b>$ is the compositional average (which is dependent on $Q$ for X-ray data) and $R_v$ is the position of atom $v$. Therefore, the single atom scattering amplitude, $\psi(Q)$, is the Fourier transform of the atomic position $R_v$ and any atom can be located by analysis of the scattered wave.

This technique is based on the same principle as Equation 2.6 in Chapter 2, which is that real space and reciprocal space are linked by a Fourier transform, in this case Equation 6.3. However, whereas a FFT of a HAADF image is a trivial process to reveal the diffraction pattern, any directly acquired diffraction pattern (data recorded in reciprocal space) cannot be reversed Fourier transformed into an atom column (real space) image. This is because in diffraction experiments $\psi(Q)$ is not measured. Instead, the intensity of the diffracted wave is measured, $|\psi(Q)|^2$. Importantly, a Fourier transform of $|\psi(Q)|^2$ can still be related to the distance between atoms, if not the actual atom positions, provided total scattering data is analysed correctly. The aim of the initial analysis was to transform the raw data into suitable total scattering data by making appropriate corrections in Gudrun.

In the total scattering experiment, the raw data collected was the summed intensity from coherent scattering, incoherent scattering, multiple scattering and background scattering, Equation 6.4. Coherent scattering is the data of most use when separated from other scattering data, therefore the remaining intensity contributions were subtracted. Background scattering was corrected by the acquisition of empty instrument and empty capillary scans. These were subtracted from the raw data in weighted proportions such that the local order from the silica capillary was removed. Multiple scattering was accounted for by scattering theory and the geometry of the sample (shape and thickness). The predominant incoherent scattering was Compton scattering, which is elastic scattering from moving electrons. This was accounted for by normalising the data to fit the profile of the structure factor, $F_{hkl}$ for Ti-15 wt.%Mo.

$$I_{\text{total}} = I_{\text{coherent}} + I_{\text{incoherent}} + I_{\text{multiple scattering}} + I_{\text{background}}$$  \hspace{1cm} (6.4)$$

The total scattering structural function $S(Q)$ is shown by Equation 6.5, where $I(Q)$ is the collected and corrected diffraction intensity over a large $Q$. Several corrections have oc-
curred during this step. For example, an absorption factor, an electric polarisation factor and a cross-section normalisation to convert the coherent intensity into a coherent scattering cross-section. In the case of normalising against $<b^2>$, a Laue monotonic scattering term is also needed to make $S(Q)$ approach unity at large $Q$, the function would otherwise approach $<b^2>$.

$$S(Q) = \frac{I(Q)}{<b^2>}$$  \hspace{1cm} (6.5)

After these corrections have been applied, the resulting total scattering data is Fourier transformed to reveal the atomic pair distribution function (PDF), $g(r)$, which is the radial probability of finding atoms separated by a distance $r$. $G(r)$ is the weighted sum of the partial $g(r)$ functions for each of the different atom species combinations, shown by Equation 6.6. In the case of Ti-15 wt%Mo, there are three partial PDF functions for each of Ti-Ti, Ti-Mo and Mo-Mo bonding. In X-ray analysis, these are weighted according to volume fraction and scattering amplitude.

$$G(r) = \sum_{i,j} c_i c_j b_i b_j (g_{i,j}(r) - 1)$$  \hspace{1cm} (6.6)

Equation 6.6 was additionally normalised by $(\sum_j c_j b_j)^2$ such that $G(r \to 0) = -1$ and $G(r \to \infty) = 0$. This was done using the program STOG contained within RMCProfile [216]. Critically, it can be shown that $S(Q)$ and $G(r)$ are related by a Fourier transform, Equation 6.7. Therefore, with high quality diffraction data to a large $Q$, very small distances can be probed. Notably, this last step can be misleading. Since $Q$ is finite, the transformation can have termination ripples throughout the spectra (being largest at low $r$). Therefore, the maximum $Q$ was carefully considered to minimise artefacts within the data. In general, the best $Q_{\text{max}}$ was found to be the largest $Q$ that satisfied $S(Q) = 0$ and $\frac{\partial S(Q)}{\partial Q} = 0$. In order to suppress any termination ripples, some data was Fourier filtered at very low distances. Again, care was taken not to disrupt the real space information by only filtering distances smaller than the nearest possible atomic distance (approximately 2.5 Å) for visual appearance. In fact, the experiment was repeated on two separate occasions as the detector in the first instance contained too high a gain at high $Q$ and low $r$ for the data to be interpreted with confidence.
6.3 The athermal $\omega$ to isothermal $\omega$ transformation.

6.3.1 Results

A 3 mm disc of Ti-15 wt.%Mo in the $\beta$ quenched state was heated to 450°C at a rate of 10°C/min while collecting DSC data and then cooled to room temperature at the same rate. The relative heat flow between the sample and reference pan for the heating (right arrow) and cooling (left arrow) is shown in Figure 6.1. On heating, no significant deviation from the baseline occurred until 200°C. At this temperature, a large endothermic transformation started. After the initial deviation at 200°C the heat flow did not return to a baseline gradient, which is an indication of a continuous change in microstructure up to the maximum experimental temperature of 450°C. In addition to the first endothermic deviation on heating, a subtle gradient change commenced at 400°C, possibly indicating a further change in the microstructure. On cooling, a continuous change in gradient occurred which possibly provides some evidence that a reversion of the microstructure was occurring which did not have time to complete.

In an RUS experiment carried out and analysed by S. Driver, parallelepipeds of Ti-15 wt.%Mo in the $\beta$ quenched state were heated to 500°C and to 850°C respectively. At each 5°C increment the natural frequencies were recorded across a frequency range and plotted as a frequency$^2$ term. The change in natural frequency for one resonant peak was selected for both samples. Whilst this peak could not be linked to a specific modulus term, it contains a representation of the change in stiffness found within the material. Figure 6.2 is a plot of the of the selected resonant peak as a function of temperature, where a shift of the resonant peak to a higher frequency$^2$ term represents an increase in stiffness. The black and red markers show the change in stiffness on heating to 500°C and to 850°C respectively. In both cases, during initial heating the stiffness was found to decrease, which may be thermal relaxation. However, the metastable $\omega$ phase also affects the stiffness. Therefore, the initial decrease could signify the dissolution of the athermal $\omega$ phase which would be present in the quenched starting condition. Critically, at 100°C the stiffness stopped decreasing and started increasing. This is an indication of a change in material structure and may correspond to $\omega$ formation. The stiffness increased to a maximum at 400°C, temperatures where isothermal $\omega$ is known to form, before reducing once more, which is likely to be the dissolution of isothermal $\omega$. 

\[
G(r) = \frac{2}{\pi} \int_0^\infty Q[S(Q) - 1] \sin(Qr) \, dQ \quad (6.7)
\]
The athermal $\omega$ to isothermal $\omega$ transformation in Ti-15 wt.%Mo

Fig. 6.1 DSC traces for heating and cooling of Ti-15 wt.%Mo from room temperature to 450°C. The starting condition is identical to that in Chapter 3 which was $\beta$ heat treated at 800°C for 1 hour followed by water quenching. The arrows indicate the heating and cooling traces respectively. A large endothermic transformation starts at 200°C and does not complete by 450°C.
6.3 The athermal $\omega$ to isothermal $\omega$ transformation.

coupled with formation of the $\alpha$ phase. Interestingly, there was no change in stiffness at the $\beta$ transus temperature ($775^\circ$C). Therefore, the resonant peak selected may be insensitive to $\alpha$ phase dissolution or formation. The blue line in Figure 6.2 corresponds to the linear increase in stiffness upon cooling from $850^\circ$C. The stiffness profile on cooling did not follow the same trend as for heating, which means isothermal $\omega$ did not form on cooling. As the resonant peak appears insensitive to $\alpha$ phase precipitation, the linear increase in stiffness may only correspond to thermal stiffening.

To understand the microstructural changes occurring from room temperature to $500^\circ$C using a direct method, a powder transmission X-ray diffraction experiment was conducted. The Bragg diffraction pattern from powder heat treated for 100 hours at $200^\circ$C, $300^\circ$C, $400^\circ$C and $500^\circ$C was measured. The results are plotted in Figure 6.3 as intensity-$2\theta$ with each temperature offset for comparison. Independent $\alpha$ and $\omega$ peaks are shown to help identify the secondary phases at each temperature. No significant difference was observed between the quenched condition and $200^\circ$C age, however, both $\beta$ and $\omega$ are present. Between 200 and $400^\circ$C, the $\omega$ reflections were sharper and more defined. At $500^\circ$C, $\alpha$ peaks have developed at the expense of the $\omega$ peaks.

The peaks attributed to the $\omega$ phase in Figure 6.3 are relatively small and diffuse. Therefore, any differences observed between the athermal and isothermal $\omega$ phase may be attributed to different sampling volumes or thermal broadening effects rather than composition. To overcome this variation, an in situ heating experiment was conducted on a separate capillary of atomised power. Within this experiment, spun powder was heated to $450^\circ$C from room temperature. At $30^\circ$C, $100^\circ$C, $200^\circ$C, $300^\circ$C, $350^\circ$C, $400^\circ$C and $450^\circ$C, the sample was held for 20 minutes at each temperature to stabilise, followed by ten minutes of data acquisition. Consequently, any variability between the temperatures is due to the changes within the material during heating and not due to experimental setup or sampling volume. An isochromic plot, containing offset scans for each temperature versus the time held at that temperature, is shown in Figure 6.4. A change in the $\omega$ peak shape can be observed in these waterfall plots. Four peaks which are only attributable to diffraction from the $\omega$ phase have been labelled 1-4 in Figure 6.4 and are seen to decrease in intensity before increasing. However, it is not immediately clear from Figure 6.4 if the change in peak height is also accompanied by a change in peak area.

To observe the change in $\omega$ peak area with temperature, all of the diffraction patterns were normalised to the beam current at acquisition. The beam current was calculated by inte-
The athermal ω to isothermal ω transformation in Ti-15 wt.%Mo

Fig. 6.2 Two overlaid RUS studies of Ti-15 wt.%Mo. The initial starting condition was 800°C for 1 hour followed by water quenching. One sample was heated to 500°C. The change in frequency² of a resonant peak with temperature is shown by the black markers. A second sample was heated to 850°C (red markers) followed by cooling to room temperature (blue markers). The frequency term relates to material stiffness.
6.3 The athermal $\omega$ to isothermal $\omega$ transformation.

Fig. 6.3 Synchrotron X-ray Bragg peaks of gas atomised Ti-15 wt.%Mo powder at room temperature following 200°C, 300°C, 400°C and 500°C heat treatments for 100 hours. Independent $\alpha$ and $\omega$ peaks are labelled to illustrate the primary second phase precipitants at each temperature.
The athermal $\omega$ to isothermal $\omega$ transformation in Ti-15 wt.%Mo

Fig. 6.4 Synchrotron X-ray Bragg diffraction patterns from an *in situ* experiment to show the evolution of the independent $\omega$ peaks. Gas atomised powder was heated to 450°C in six steps. Ten diffraction patterns were acquired at 30°C, 100°C, 200°C, 300°C, 350°C, 400°C and 450°C. On reaching each temperature, the material was allowed to thermally stabilise for 20 minutes prior to data acquisition. The scans are uniformly offset in the y-axis to show the evolution of Bragg peaks over this heating period. The four peaks indicated are $\omega$ peaks which are independent from the $\beta$ peaks.
6.3 The athermal ω to isothermal ω transformation.

The normalised peak area for the four ω peaks indicated in Figure 6.4. The error bar indicates the standard deviation in peak area found between the ten scans taken at each temperature.

In addition, the \{110\}_β peak was masked to prevent any data skew that may be induced by the clipping of the most intense peak. The area under each ω peak was calculated by integrating the intensity over an angular range, followed by a linear subtraction of the background over the same range. To compare the peak intensities between different ω reflections, the data was also normalised against the room temperature result. The ω peak areas as a function of temperature are plotted in Figure 6.5. The error bars on the plots are included to show the standard deviation across the ten scans at each temperature. There was very little variation over the ten, one minute scans, which suggested the 20 minute temperature stabilisation period was sufficient. Significantly, on heating, the peak area reduced between room temperature and 100°C before increasing to a maximum at 400°C and following a similar trajectory to that in Figure 6.2. Between 100°C and 200°C there was a discrepancy. The ω peaks labelled 1 and 3 increased in peak area whilst peaks 2 and 4 decreased. This means the data had to be more robustly treated.
The athermal $\omega$ to isothermal $\omega$ transformation in Ti-15 wt.%Mo

Fig. 6.6 A unit cell with P-3m1 symmetry viewed along [0001]$_{\omega}$ (or <111>$_{\beta}$) showing the atom positions for perfect $\beta$ and ideal $\omega$ phases. For perfect $\beta$ the atoms are located at 0,0,0, 2/3,1/3,1/3 and 1/3,2/3,2/3. For ideal $\omega$ the atoms are located at 0,0,0, 1/3,2/3,1/2 and 2/3,1/3,1/2. The unit cells can generated using P-3m1 symmetry with positions 0,0,0 and 2/3,1/3,1/3+Z. Where Z=0 for perfect $\beta$ and 1/6 for ideal $\omega$.

One method of understanding phase transformations from diffraction data is by least squares fitting the whole diffraction pattern to a model. A model can consist of one or more phases defined by unit cell symmetry, lattice parameters, occupancies and fractional coordinates. A wide variety of variables can then be refined to fit the model to the experimental data. In order to fit the model, the first diffraction pattern for each temperature in the 30-400°C range was taken, corresponding to patterns which only contain $\beta$ and $\omega$. These patterns were initially fitted to the parent $\beta$ phase. The $\beta$ phase was best described by the Im-3m BCC symmetry group with Ti and Mo atoms at 0,0,0 in 0.92 and 0.08 atomic fraction proportions. The $\omega$ phase was then included. The $\omega$ structure can be described using P-3m1 symmetry (trigonal) with atom positions at 0,0,0 and 2/3,1/3,1/3+Z. The trigonal P-3m1 cell for $\omega$ is shown in Figure 6.6. When Z is 0 the structure is identical to cubic Im-3m, which is the symmetry group for the $\beta$ phase. When Z is 1/6, the symmetry is P6/mmm which corresponds to a hexagonal $\omega$ structure. Therefore, Z is an indication of the $\{111\}_{\beta}$ displacement along <111>$_{\beta}$ and is 1/6 for ideal $\omega$ and 0 for perfect $\beta$.

When fitting diffraction data to a model, the fit can depend on the model used. In this case, there are two possible ways of modelling a system containing the $\beta$ and $\omega$ phases. The first model is a two phase model that fits the data to the perfect $\beta$ and ideal $\omega$ structure. The critical variables in this case are the volume fractions of the two distinct phases and their compositions. Fitting constraints were set up to enable the decrease in Mo concentration in the $\omega$ phase to correspond to an increase in the Mo concentration in the $\beta$ phase, with
The athermal ω to isothermal ω transformation. The second model used to fit the diffraction data used a single phase to describe both the β and ω structures together. Within Chapter 4, the athermal ω phase was found to be best described as the β phase with a frozen phonon. Therefore, the average structure could be described by P-3m1 where Z takes a value between 0 and 1/6. Since only one phase was used in this model, the composition had to remain at the nominal Ti-15 wt.%Mo composition. Therefore, only the lattice parameters and Z were refined. Ideally, the Z values for the Ti atoms and the Mo would be independently refined to see if the extent of collapse varied between the two species. However, although the software can set up this condition, the fits became very unstable and failed to converge. Importantly, this second model contained fewer variables to refine than the two phase model.

The GSAS fits of the single phase and two phase models to the experimental data are shown in Figure 6.7 for 30°C, 100°C, 200°C, 300°C and 400°C. The residuals (the difference between the fit and model) for both models are shown offset beneath the diffraction data. At all temperatures and for the two different models, the residual showed a good fit for a Rietveld fit of metallic material. This is because powder was used rather than material cut directly from the extruded bar which would contain preferential orientation. Across all fits, the residual is largest for the {110}β peak at 4°. This is probably because this peak is the most intense and might possibly have been clipped by the detectors approaching saturation after a minute of exposure. Significantly, for all cases, the one phase model contained a similar fit to the two phase model, making both models valid for describing the quenched and heated structures.

After the satisfactory fit was achieved between model and experimental data, as shown in Figure 6.7, information can be determined about the system by consideration of the refined model parameters. For the two phase fit, the volume fraction and the composition of the ω phase can be extracted for each temperature, Table 6.3. Critically, the concentration of Mo within the ω phase initially decreased slightly on heating whilst the volume fraction of the ω phase increased. Both of these factors support the precipitation of isothermal ω on heating from room temperature. In contrast, the results from the single phase fit disagreed. Table 6.4, which shows the change in Z with temperature, indicated the average extent of {111}β collapse remained constant (and may have possibly decreased slightly) until 200°C, followed by the development of the ω structure between 300 and 400°C. This inferred that from a long range coherent standpoint, there was no significant change in the ω structure until between 200 and 300°C. Therefore, these findings suggest that Bragg data alone cannot
The athermal $\omega$ to isothermal $\omega$ transformation in Ti-15 wt.%Mo

Fig. 6.7 Diffracted X-ray intensity for scans acquired at 30°C, 100°C, 200°C, 300°C and 400°C over a small angular range. Data points are marked by solid circles. Acquired data fitted using whole pattern Rietveld fitting to two structures; P-3m1 and Im-3m + P6/mmm. The residuals between experimental data and model fits are offset and shown below the data.
convincingly establish the mechanism of structural alteration.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Volume fraction of ω (%)</th>
<th>at.% Ti in the ω phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>14.4 +/- 0.3</td>
<td>92.0</td>
</tr>
<tr>
<td>100</td>
<td>15.6 +/- 1.6</td>
<td>96.3</td>
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<tr>
<td>200</td>
<td>18.2 +/- 1.7</td>
<td>96.5</td>
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<tr>
<td>300</td>
<td>25.1 +/- 2.5</td>
<td>92.9</td>
</tr>
<tr>
<td>400</td>
<td>35.9 +/- 4.5</td>
<td>93.0</td>
</tr>
</tbody>
</table>

Table 6.3 Full pattern Rietveld fit using Im-3m and P6/mmm structures.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Z</th>
<th>at.% Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.034</td>
<td>92.0</td>
</tr>
<tr>
<td>100</td>
<td>0.031</td>
<td>92.0</td>
</tr>
<tr>
<td>200</td>
<td>0.030</td>
<td>92.0</td>
</tr>
<tr>
<td>300</td>
<td>0.047</td>
<td>92.0</td>
</tr>
<tr>
<td>400</td>
<td>0.065</td>
<td>92.0</td>
</tr>
</tbody>
</table>

Table 6.4 Full pattern Rietveld fit using P-3m1 structure refining the extent of collapse, Z.

A new X-ray diffraction analysis approach was taken to incorporate all possible sources of structural information, both diffuse and Bragg scattering, to try and establish which possible structural evolution pathway was actually occurring. Figure 6.8a contains the scattered intensity from a powder sample at room temperature after a ten minute total exposure. Only one quarter of the detector is shown as the rings are continuous around the central beam stop. The data used for the Rietveld analysis was the same data as used for total scattering. However, in the Rietveld analysis, only the first five rings were used. The intensity in Figure 6.8a is plotted on a log scale to show the presence of scattered intensity to high $Q$, which means the inclusion of 25 or more rings of scattered intensity can be used. The total 2D scattering data was radially integrated around the centre and corrected for sample absorption, self scattering and Compton scattering using the designated X-ray Total Scattering reduction program Gudrun, as discussed in the Section 6.2.7. The resultant scattering structure function $S(Q)$ is shown in Figure 6.8b. The insert in Figure 6.8b emphasises the Bragg and diffuse information at high angle is above background noise due to the long acquisition time and the quality of the detector.

The Fourier transform of Figure 6.8b is plotted in Figure 6.9. In theory, the ω phase is contained within the entire PDF and can be separated from the β phase. However, it
Fig. 6.8 a) One quarter of the Debye-Scherrer rings acquired using the 2D Pixium detector in a Total Scattering setup. b) The full radial integration of the detector intensity plotted as a function of Q. The high Q intensity is highlighted within the insert to show high quality data was collected to a high Q.
was uncertain whether this information could be isolated entirely due to instrument error contributions, processing effects and thermal contributions. To identify unique $\omega$ radial distances, the experimental PDF data was compared to calculated PDF data for the perfect $\beta$ structure and ideal $\omega$ structure. The comparison between room temperature experimental PDF data (symbols) and simulated PDF data (line) is shown in Figure 6.10a & b. Perfect $\beta$ and ideal $\omega$ structures would have peaks of negligible width. However, above 0 K atoms would always contain isotropic thermal displacements. Therefore, the atom positions in each of the simulated structures were randomly displaced in three-dimensions. When comparing the simulated PDF data between perfect $\beta$ and ideal $\omega$, the number of peaks in the ideal $\omega$ structure, Figure 6.10b, is greater than for perfect $\beta$, Figure 6.10a. It can also be seen that many of the PDF peaks overlap. This is not surprising due to the similarity between the two structures. However, at 3.9 Å there is an isolated and independent $\omega$ peak.

Fig. 6.9 The Fourier transform of the structure factor in Figure 6.8 to yield the PDF.
The athermal $\omega$ to isothermal $\omega$ transformation in Ti-15 wt.%Mo

Fig. 6.10 Comparing the experimental PDF data to modelled: a) perfect $\beta$, b) ideal $\omega$, c) a two phase 0.85$\beta$ + 0.15$\omega$ model and d) frozen phonon description.
Within Figure 6.10a & b the experimental PDF did not closely relate to either the perfect $\beta$ structure or ideal $\omega$ structure. This was not surprising as it had been previously shown that the quenched material contains both the $\beta$ and athermal $\omega$ structures. However, comparing the room temperature experimental data with a two phase model did not significantly improve the fit. This is shown in Figure 6.10c which included contributions from 15% ideal $\omega$ randomly dispersed amongst a $\beta$ matrix. In addition, no better fit could be found by changing the percentage of ideal $\omega$. In contrast, the single phase simulation in Figure 6.10d contained a very reasonable fit to the experimental data. In this case, the $\beta$ phase was simulated with the addition of a frozen phonon in the $<111>_\beta$ towards the $\omega$ structure. Therefore, whilst the two treatments of $\beta$ and $\omega$ produced similar fits in the Bragg analysis, Figure 6.7, the single phase fit in the total scattering analysis was superior. This is reasonable since Bragg analysis removed background contributions resulting in the loss of important diffuse phonon contributions that describe the structure.

Critically, there is an independent $\omega$ distance at approximately 3.9 Å in the PDF. This peak was used to observe the change in structure associated with the $\omega$ phase on heating from the as-quenched condition. The same powder was used during the heating experiment to minimise any potential variation between different samples. The spun capillary of Ti-15 wt.%Mo powder was heated using a gas blower. At 30°C, 100°C, 200°C, 300°C and 400°C the powder was left to thermally stabilise for 20 minutes followed by ten minutes of acquisition. The total scattering data on heating were processed to give the structure function for each temperature. As the only variable on heating was temperature, the correction parameters were kept constant between the different temperatures. This limited the processing error when comparing the PDFs at different temperatures. The Fourier transforms of the corrected data for each of the temperatures are shown in Figure 6.11a. As the differences seen between the temperatures are small, no Fourier filtering was conducted to clean the truncation ripples. This correction may have affected the profiles differently depending on the level of thermal noise at $Q$ max. The $\omega$ specific distance at 3.9 Å is expanded and shown in Figure 6.11b, with the temperature for each PDF indicated. At all temperatures, there was intensity at 3.9 Å which indicated atoms in the $\omega$ structure. In addition, the number of atoms at the 3.9 Å positions varied with temperature. From 30°C to 200°C the PDF trace decreased followed by a dramatic increase between 200°C and 300°C. An increase was also observed at 400°C. However, it was also noted that a maxima is present at 400°C. The implication of this is that the traces between 30°C and 300°C closely resemble the simulated structure in Figure 6.10d whereas the experimental trace at 400°C matched the simulated structure in Figure 6.10c.
The athermal \( \omega \) to isothermal \( \omega \) transformation in Ti-15 wt.%Mo

Fig. 6.11 a) Overlay of PDF traces for 30°C, 100°C, 200°C, 300°C and 400°C. b) \( \omega \) specific distance is expanded.

6.3.2 Discussion

The aim of the experimental work carried out here was to better understand the athermal to isothermal \( \omega \) transformation. This was conducted by several direct and indirect experiments that investigated the \( \omega \) phase during in situ and ex situ thermal exposures. An attempt to explain the DSC (Figure 6.1) and RUS (Figure 6.2) curves can be made based on the results obtained from samples bulk heat treated for 500 hours reported in Table 3.3 in Chapter 3 and the 100 hour powder heat treatments that were carried out in this chapter (Figure 6.3). The in situ trends from the DSC and RUS experiments are entirely consistent with the precipitation of the isothermal \( \omega \) phase reaching a maximum volume fraction at 400°C. In particular, the decrease in stiffness between 400°C and 500°C could be the dissolution of \( \omega \) and formation of \( \alpha \). Critically, it is recognised that the sharpening of diffuse \( \omega \) peaks, the change in stiffness and the change in heat flow with temperature is directly comparable with the \( \omega \) phase evolution observed in Chapters 3, 4 and 5 and is in-line with reviews of isothermal \( \omega \) formation [22, 30]. Significantly, a change in alloy stiffness was observed between 30 and 200°C that is consistent with ultrasonic studies of Timetal LCB (which is based on the Ti-Mo binary) [56]. In both Ti-15 wt.%Mo and Timetal LCB, the stiffness reduced from room temperature to a minima at 180°C. The subsequent increase in stiffness is most likely isothermal \( \omega \) precipitation which reinforces the matrix due to lattice missfits. Therefore, 180°C could signify the start of long range Mo diffusion and the isothermal \( \omega \)
start temperature. However, the cause of the decrease in stiffness between room temperature and 180°C cannot be deduced since it may either be thermal relaxation or the dissolution of athermal ω [54, 59, 71]. Therefore, complementary information is essential.

Synchrotron X-ray diffraction data, such as that in Figure 6.3 can be used to deduce quantitative information about the structures and compositions of the phases present. This is because a powdered sample has good grain statistics resulting in continuous sampling across all grain orientations, regardless of the phase size. Consequently, peak intensities can be used to determine the volume fractions and atomic coordinates of the phases at each temperature. This is critical to understanding the athermal to isothermal ω transformation between 30 and 400°C.

Here, it was found that the analysis of ω peak area, Figure 6.5, followed a similar trend to the RUS data, Figure 6.2. However, analysis under 200°C gave different results depending on which ω peak was investigated. This contradiction in behaviour means the data may not have been robustly treated. For example, the linear background subtraction over the peak range may be inappropriate when considering the nature of diffuse peaks. A better method of determining phase information from the diffraction data is to undertake a full pattern analysis which takes into account the β phase. Specifically, the better the diffraction peaks can be described together, the more information can be ascertained about the athermal to isothermal ω transformation. Critically, the data acquired was of high enough quality for the experimental data to be fitted to models of the β and ω structures, Figure 6.7. However, it was possible to fit two conflicting model explanations for the athermal to isothermal ω transformation from the same X-ray data. Importantly for this analysis, the results were largely dependent on the initial assumptions about the system and the ability to fit the model to the data. It could be argued that the single phase fit was more representative of the starting condition, since it has been shown in Chapter 4 that the frozen phonon model (single phase model) better predicts the experimental images than the block model (two phase model). However, in this X-ray diffraction study, the single phase fit was slightly worse than the two phase fit. This could be because the two phase model contained more variables that could be refined, which enabled a better fit to be achieved. It was not possible to distinguish between the appropriateness of these two models based on this data alone and with the assumptions used here.

Both the full diffraction pattern phase analysis and the separate ω peak considerations shared a common treatment of data. In both cases, only coherent Bragg diffraction data were consid-
The athermal \( \omega \) to isothermal \( \omega \) transformation in Ti-15 wt.%Mo

The area beneath the Bragg peaks was not considered in the analysis and background data were subtracted using an empirical background formula. For example, a linear function was used to remove the background in the single phase peak analysis, whilst a 20 order shifted Chebyshev was used in the full pattern fits. Whereas the background data contained undesirable noise contributions, it also contained some diffuse information. The connection between the \( \omega \) phase and thermal diffuse components has already proven to be important in understanding of the \( \omega \) structure using results from electron scattering experiments in Chapter 4. Therefore, a full consideration of the X-ray data without empirical subtractions was required. This was achieved by total scattering analysis, such as in Figure 6.8 and Figure 6.9.

Figure 6.9 is the PDF for the as-quenched material and is a weighted sum of the radial probability of finding Ti-Ti, Ti-Mo and Mo-Mo atoms separated by the distance \( r \). Significantly, Figure 6.9 contains real space information as to the positions of atoms in the as-quenched material. Within Figure 6.9 all intensities contain contributions from Ti-Ti, Ti-Mo and Mo-Mo partials weighted according to the composition. Therefore, the PDF can be used to extract a multitude of structural and compositional information. However, the radial distributions of atoms in the \( \beta \) and \( \omega \) phases are similar, resulting in overlapping peaks, Figure 6.10a & b. In addition, peak broadening at higher \( Q \) due to instrument resolution and phonon effects can widen the peaks and make them more difficult to deconvolve. It was therefore important to find a radial distance at a low \( r \) which was unique to the athermal \( \rightarrow \) isothermal \( \omega \) phase transformation.

Figure 6.12 is schematic representation of a \{110\}_\beta plane of atoms. The first six nearest neighbours are indicated in a region containing the perfect \( \beta \) structure. In a PDF plot, this would correspond to a peak at each of the six \( \beta \) distances. As demonstrated in Chapter 4, the \( \omega \) structure can be described as the perturbation of \( \beta \) structure where two-thirds of the \{111\}_\beta are collapsing, meaning the nearest neighbour distance in the \( \omega \) structure (both trigonal and hexagonal descriptions) is smaller than in the ideal \( \beta \) structure. This would mean an additional peak in the PDF plot would occur at a smaller distance than the first \( \beta \) peak. However, in this case, first nearest neighbour analysis is difficult because these peaks are sensitive to noise at high \( Q \) during acquisition, thermal vibrations, termination ripple effects, incorrect corrections, Fourier filters, \( Q_{\text{max}} \), detector clipping and texture. All of these many effects can change the signal at low \( r \). Therefore, although this smallest distance could potentially supply key information about the collapsing, it was not practical to consider this in the analysis. The same nearest neighbour peak also occurs at multiples of this closest
6.3 The athermal $\omega$ to isothermal $\omega$ transformation.

Fig. 6.12 A $\{110\}_\beta$ highlighting how the radial distribution between atoms will be different between the $\beta$ and $\omega$ structures. Two variants of the $\omega$ phase are given.

distance. However, as shown in Figure 6.9, different variants of the $\omega$ phase exist. Therefore, it can be seen that after only a few orders of neighbours, the radial peaks from one variant can overlap with another variant and will further complicate analysis.

Significantly, from Figure 6.10 it was established that there is no contribution to the PDF from the perfect $\beta$ structure at 3.9 Å (Figure 6.10a). However, at 3.9 Å there is a significant peak relating to the $\omega$ structure, Figure 6.10b. This distance is therefore an isolated and independent $\omega$ specific distance between atoms in three-dimensions.

Within the Bragg analysis results, two models of the $\beta$ and $\omega$ phases were investigated and both gave a similar fit, which meant no discrepancies between the two models could be found. The equivalent PDFs for the two models were calculated and compared to the experimental PDF data in 6.10c & d. Whilst the two phase model might be a slightly better fit in the Rietveld Bragg analysis, the single phase phonon PDF better fits the PDF experimental data, 6.10d. In particular, at 3.9 Å the shape and intensity of the calculated phonon PDF better matched the two phase PDF. This result is in agreement with the results from the multi-slice simulations of electron HAADF images in Chapter 4.

Without making any structural assumptions, the total scattering technique enabled the athermal $\omega$ to isothermal $\omega$ transformation to be better understood. An important observation from Figure 6.11b is that for all temperatures between 30°C and 400°C, there is always a probability of finding atoms separated by 3.9 Å; i.e. the $\omega$ phase is present at each temperature. Therefore, there was no evidence for complete dissolution of athermal $\omega$ prior to isothermal
ω formation. In addition, the PDF trace is similar between the simulated data in Figure 6.10c and experimental data from 400°C shown in Figure 6.11 as well as simulations in Figure 6.10d and experimental data at 30-300°C in Figure 6.11. This is an indication of the transformation from a frozen phonon description to one of ideal ω contained within perfect β. Consequently, both single and two phase Rietveld Bragg models could be correct but at different temperatures.

The relative heights of the PDF signals in Figure 6.11b remain an intriguing question. The lowering of signal may be interpreted as a decrease in the proportion of the ω phase present. However, it is also known that the ω phase rejects Mo into the β matrix shown in Chapter 3. Whilst the reduction in volume fraction and loss of Mo from ω peaks in Bragg analysis may correspond to a reduction in peak area, the interpretation is more complex in PDF analysis. This is because the weighted contributions of Ti-Ti, Ti-Mo and Mo-Mo in the two phases will be different. Importantly, if the effects of composition and local structure can be separated in the analysis, the nature of the transformation could be determined. For example, it is currently unknown if the displacement component happens before the diffusion component or if the transformation is a displacement-diffusion mixed mode [2]. Therefore, PDF analysis may be a very helpful in solving this question.

A plot of the weighted contribution of the Ti-Ti, Ti-Mo and Mo-Mo bonds towards the PDF signal as a function of alloy composition are shown in Figure 6.13. More ω atoms mean a higher signal at 3.9 Å. However, as Mo atoms leave the ω structure they are replaced by Ti atoms. As shown in Figure 6.13, a higher concentration of Ti will cause the PDF signal to become more dependent on the Ti-Ti bond. Therefore, the ω signal weight may decrease. The balance between ω formation and Mo rejection is certainly responsible for the change in signal between 30°C and 450°C in Figure 6.11 and will need more involved techniques to be understood. Reverse Monte Carlo analysis (using RMCPProfile [216]) of PDF data is a very powerful tool for understanding local order in material [8]. Specifically, a large box of simulated Ti and Mo atoms in the β and ω structures could be simultaneously fitted, through a Monte Carlo method, to the Bragg data, structure factor function and PDF. Therefore, the subtle changes in Figure 6.11 may be extracted by examining the positions and species distribution of simulated boxes of Ti and Mo atoms. However, rigorous two phase fitting in RMCPProfile is currently beyond the capability for simulating the nuances of the athermal to isothermal ω transformation. Preliminary attempts of this are included in Chapter 8.
Fig. 6.13 The contribution of the Ti-Ti, Ti-Mo and Mo-Mo bonds to the PDF as a function of composition. Ti-15 wt.%Mo is marked by the dotted line.
6.4 Chapter conclusions

The athermal to isothermal $\omega$ transformation was investigated in $\beta$ quenched Ti-15 wt.%Mo using a myriad of direct and indirect tools to understand the small microstructural changes on heating. Here, for the first time, in situ total scattering data was collected in conjunction with other conventional in situ methods including coherent X-ray scattering, DSC and RUS. It was found that:

1) The stiffness of the alloy decreased between room temperature and $180^\circ$C. This observation was attributed to thermal softening of the $\beta$ matrix and not the dissolution of the athermal $\omega$ phase. Based on the evidence provided here, the $\omega$ phase can still be described using a frozen phonon model that incorporates partial \{111\}$\beta$ collapse between these temperatures. Some short range diffusion may occur at these low temperatures, resulting in the decrease in PDF $\omega$ signal, and is most likely local rejection of Mo atoms from locations that contain an $\omega$ structure close to that of ideal $\omega$.

2) Between $180^\circ$C and $200^\circ$C discrete isothermal $\omega$ precipitates formed. At this temperature, long range diffusion had possibly activated, which facilitated the nucleation of the isothermal $\omega$ in preference to $\alpha$ due to the presence of existing athermal $\omega$ heterogeneous sites.

3) Between $200^\circ$C and $400^\circ$C isothermal $\omega$ increased in size and volume fraction. In addition, the average \{111\}$\beta$ collapse moved from a single phase $\beta$ frozen phonon description to a two phase ($\omega + \beta$) description.

4) Beyond $400^\circ$C the volume fraction of $\omega$ decreased and there was a corresponding increase in the $\alpha$ phase. On returning back to $400^\circ$C the isothermal $\omega$ re-precipitated, which emphasises the pseudo-equilibrium nature of isothermal $\omega$.

Strictly, within the athermal to isothermal $\omega$ transformation, if Mo is redistributing at a temperature between room temperature and $180^\circ$C then the $\omega$ phase cannot be described as athermal by definition. Therefore, although long range diffusion is apparently activating at $180^\circ$C, the isothermal $\omega$ start temperature may be lower. Consequently, chemical changes possibly preceded structural changes even though the structural change is temperature independent. Therefore, the athermal $\omega$ to isothermal $\omega$ transformation will be very dependent on which $\beta$ stabilising elements are present since diffusivities will vary.
Chapter 7

Conclusions

The aim of this PhD project was to investigate the strengthening of metastable $\beta$ titanium alloys by fundamentally understanding the stability and transformation pathways which make this alloy class unique. In particular, the decomposition of the $\beta$ phase in conjunction with the formation of stable and metastable product phases makes this system both versatile and complex. This complexity was found to be apparent even in the simple binary isomorphous Ti-Mo system and specifically the Ti-15 wt.%Mo alloy studied here. Therefore, a myriad of complimentary techniques were used for each aspect studied to isolate and confirm the observations made. This section contains the conclusions drawn across each of the experiments undertaken to further the understanding of this intriguing class of titanium alloys.

7.1 Phase stability and element partitioning

The first objective of this thesis was to characterise phase stability and elemental partitioning of Ti-15 wt.%Mo following long duration thermal exposures with the aim of finding evidence for a spinodal decomposition. This is because within the isomorphous Ti-Mo system binary phase diagram there was contention that this system contained a monoeutectoid reaction which would lead to a spinodal decomposition [116]. In this work, Ti-15 wt.%Mo was heat treated at -263, 30, 100, 200, 300, 350, 400, 450, 500, 600, 700, 800, 785, 875 and 975°C following water cooling from the $\beta$ phase field. All of these thermal treatments were for times between 30 minutes to 500 hours. Despite the in-depth studies, including both EDX and EELS, into the possibility of chemical alteration, no evidence for a spinodal decomposition of the $\beta$ phase was found following heat treatment at any of these temperatures.
Despite the lack of evidence found for a spinodal decomposition, no solid conclusion can be made whether the Ti-Mo phase diagram contains a spinodal decomposition because there are arguments for and against the expectation of Ti-15 wt.%Mo to undergo this transformation. On one hand, according to the phase diagram in Figure 2.14, a monoeutectoid in Ti-Mo would not be expected below 20 wt.%Mo. Conversely, it can be argued that $\beta$ spinodal decomposition will only occur below 25 wt.%Mo when the $\beta$ phase is metastable. Therefore, the only conclusion that can be drawn is that the $\beta$ phase in Ti-15 wt.%Mo does not appear to undergo a spinodal decomposition. Consequently, the athermal $\omega$ reported in this work in Ti-15 wt.%Mo is unlikely to have formed by the same novel mixed-mode transformation reported in Ti-18 wt.%Mo since this transformation relies upon the presence of a spinodal decomposition.

Rather than a spinodal decomposition of the $\beta$ phase, the product phases observed were instead attributed to the athermal $\omega$, $\alpha$, isothermal $\omega$ or B2 phases. These phases are shown in Figure 7.1a-d, which is a showcase of the fine and homogeneously distributed product phases found within this work. In general, due to the fine and homogeneous nature of these secondary phases, spectroscopy was difficult and required near-simultaneous EELS acquisition to identify the B2 phase and principle component analysis for sub-nanometer atom column chemical resolution. However, the EDX and EELS results added credibility to the observations made when imaging features in the microstructure. For example, for the first time, the composition of isothermal $\omega$ phase was quantified using STEM EDX following 500 hours at 400°C. It was found that the $\omega$ precipitates rejected all but 0.8 wt.%Mo. Significantly, this value is close to the amount of Mo contained within the $\alpha$ precipitates and is lower than reported in literature. A survey of results obtained using atom probe tomography claim concentrations around 4 wt.%Mo [30, 64]. However, it could be argued that the results reported here are more likely to be equilibrium concentrations since the alloys were heat treated for 500 hours rather than just a few minutes or hours. This is especially significant since Mo diffusion in Ti is thought to be slow and isothermal $\omega$ precipitation only occurs below 400°C. Therefore, it is concluded that phase stability and element partitioning in Ti-Mo may be less contested following further studies containing equally long thermal exposures and chemical analysis techniques.

### 7.2 Nature of the athermal $\omega$ phase

The second aim of this thesis was to investigate the possibility of local structure and the nature of the athermal $\omega$ phase in material quenched from the $\beta$ phase field. Critically, there
Fig. 7.1 Raw electron microscope images of product phases found within the parent $\beta$ phase. a) $\beta + \omega_{\text{ath}}$, b) $\beta + \alpha$, c) $\beta + \omega_{\text{iso}}$ and d) $\beta + \text{B2}$. Note the change in scale bar from 500 pm to 50 nm.
Conclusions

is an ambiguity between the static and dynamic theories of athermal \( \omega \) formation in the literature. Whilst no chemical alterations were found in athermal \( \omega \), this alone cannot be used to prove or disprove either theory. Instead, significant advances in the study of athermal \( \omega \) formation were made through the consideration of both incoherent and coherent observations. Importantly, although the interpretation of incoherent observations may be more intuitive, it is clear that even when incoherent measurements are made, these measurements require the same degree of interpretation and scientific scrutiny as historically done for coherent observations. Specifically, comparing experimental results to simulations resulted in evidence to support the dynamic theory of athermal \( \omega \) formation.

In this work, two approaches were used to measure the incoherent and coherent scattering from \( \beta \) quenched material and both approaches were supported with simulations. These methods were electron ADF HR-STEM imaging and Total Scattering of X-rays. For the former method, it was observed that atom column appearance differed when simultaneously observing the same region of material in coherent and incoherent detector setups, LAADF and HAADF respectively. This was further developed to isolate regions containing the athermal \( \omega \) phase and observe the tri-layer periodicity over a range of inner collection angles. It was observed that the tri-layer periodicity changed when the proportion of coherent to incoherent signal was altered between images. Critically, multi-slice simulations showed the switch in tri-layer periodicity to occur at different inner collection angles depending on how the athermal \( \omega \) phase was simulated. It was found that simulations of the dynamic theory of athermal \( \omega \), which describes the metastable phase to be a frozen phonon of the \( \beta \) phase, best matched the experimental ADF observations.

Whilst the X-ray Total Scattering method is not new, this work reports the first use of PDF analysis of a metastable \( \beta \) titanium alloy. From the multi-slice electron simulations it was concluded that plane collapse in the athermal \( \omega \) phase may not be complete, with each unit cell of the \( \omega \) cell containing a different extent of \( \{111\}_\beta \) collapse. This conclusion is supported by X-ray total scattering analysis of athermal \( \omega \), which showed the PDF signal to best match a box of simulated atoms containing a frozen phonon. Therefore, it is concluded that at high temperatures the \( \{111\}_\beta \) are continually collapsing and un-collapsing with the soft phonon and that the position of all the atoms are frozen in place upon fast cooling from the \( \beta \) phase field.
7.3 The isothermal \( \omega \) phase and the \( \omega_{\text{ath}} \to \omega_{\text{iso}} \) transformation

The third objective of this thesis was to explore the athermal to isothermal \( \omega \) phase transformation using in situ and ex situ techniques. The aim was to determine if the athermal \( \omega \) dissolved prior to isothermal \( \omega \) formation. It was found that the transformation could be recorded using several methods such as DSC, X-ray diffraction and RUS but the interpretations from these experiments could only be inferred by the ex situ studies. It was also difficult to draw conclusions as these techniques depended on the assumptions made about the transformation. However, total scattering and PDF analysis requires fewer assumptions about the transformation. The only assumption made was that the changes in the \( \omega_{\text{ath}} \to \omega_{\text{iso}} \) transformation would be small and therefore the data acquired at each interval could be treated in the same way. This is reasonable as the small changes involved are what cause this transformation to be in contention. Critically, it was found that the \( \beta + \omega_{\text{ath}} \to \beta \) did not occur in full. It is possible that the volume fraction of the athermal \( \omega \) may have decreased but this could not be determined directly as random fluctuations in the Mo distribution may complicate interpretation. By combining the conclusions from RUS and PDF experiments, there is strong evidence that the start temperature of isothermal \( \omega \) is between 180\(^\circ\)C and 200\(^\circ\)C. This is important for alloy design as products in service above this temperature may exhibit a change in properties over time.

7.4 Thin foil artefacts and a new phase in Ti-15 wt.%Mo

During the study of the three primary aims, several unexpected results were found. In general, high resolution microscopy and spectroscopy is benefited by using thin electron transparent material. This enabled atom column resolution of the athermal \( \omega \) phase without the need for filtering or image corrections which therefore give the observations validity. However, a downside was discovered when studying thin films of \( \beta \) quenched Ti-15 wt.%Mo as thin foil artefacts were observed which were not representative of the bulk. For example, the lath-like features observed contained the same appearance as martensite but the corresponding diffraction data was absent. Surface examinations showed surface buckling, indicative of a compressive strain. Ti-15 wt.%Mo may contain a residual stress of up to 1 GPa upon \( \beta \) quenching due to the formation of athermal \( \omega \) phase imparting a stress into the matrix as a result of a lattice parameter mismatch [5]. On thinning, this stress may have been relieved in compression resulting in twin formation and buckling. This work identified \{112\}<111>\( _{\beta} \)
twins and showed that the twin pattern can contain near-identical diffraction patterns to stress induced $\omega$ if double diffraction is also present. This observation was appreciated in the early studies [65] but may have been misinterpreted in subsequent studies. However, stress induced $\omega$ may still be plausible in twin formation since a twin interface could locally be interpreted as a twin structure. Therefore, both high and low resolution TEM techniques may be required to understand the nature of any deformation products and artefacts observed in the production of thin foils for analysis.

One concern was that these lath-like artefacts may have altered the nature of the athermal $\omega$ phase, making the HAADF frozen phonon conclusions invalid. However, as previously stated, many of the observations were made using several complementary techniques. Therefore, this concern was reduced as the same conclusions about the athermal $\omega$ phase were made from the total scattering experiments, which did not use thin material.

A second unexpected result was found when $\beta$ quenched material was heat treated in the thinned condition. On heating thin $\beta$ quenched material to 300°C, a new structured phase was discovered. This ordered $\beta$ phase contained a B2 structure which has never been reported within Ti-15 wt.%Mo alloy or even within the Ti-Mo system. By combining *in situ* and *ex situ* studies, it was conclusively shown that this phase was not representative of the bulk material.

### 7.5 Summary

In summary, this work was a study of the omega phase in Ti-15 wt.%Mo. The key conclusions from this section are made below:

- The $\beta$ phase in Ti-15 wt.%Mo showed no evidence for a spinodal decomposition. Therefore, the novel mixed mode theory of athermal $\omega$ formation in Ti-15 wt.%Mo may not necessarily apply.

- Tri-layer periodicity observed in HAADF images was found to be the effect of two phases along the beam path and not due to local site occupancy.

- A new HR-STEM tool for studying the $\omega$ was explored. It was found that inner collection angles are an important parameter when interpreting the $\omega$ phase. Using this, it was found that the athermal $\omega$ was best described using the dynamic frozen phonon theory.
• Two artefacts have been observed in Ti-Mo thin films; a newly discovered B2 phase in Ti-15 wt.%Mo and \{112\}<111>$_{\beta}$ twinning.

• Total scattering provided further evidence that the athermal $\omega$ phase is best described by a frozen phonon.

• Heating quenched Ti-15 wt.%Mo showed the retention of the athermal $\omega$ phase before the precipitation of the isothermal $\omega$ phase. Mo diffusion was found to occur around 200°C, signifying the start of isothermal $\omega$ precipitation.
Chapter 8

Further Work

8.1 The Ti-Mo system

During this project, Ti-15 wt.%Mo was investigated at temperatures ranging from the solidification temperature (atomised powder) to -263°C (neutron diffraction). No evidence for spinodal decomposition was found across the multiple techniques and temperatures employed. However, the presence of a mono-eutectoid reaction in the Ti-Mo binary could not be discounted based on the fact that Ti-15 wt.%Mo may be too lean to contain this transformation. It is therefore suggested that several Ti-Mo alloys spanning the Ti-Mo system should be characterised with respect to phase stability and elemental partitioning following long duration thermal exposures. As a preliminary investigation into this, a series of Ti-Mo alloys were manufactured using an induction arc melter by N. Jones. Ti-25 wt.%Mo, Ti-45 wt.%Mo and Ti-60 wt.%Mo alloys were made by melting and re-melting Ti and Mo feedstock in the appropriate proportions until a homogeneous bar was produced. The bars were then encapsulated under an argon atmosphere and heat treated for 500 hours at 800°C. SEM-EDX, XRD and TEM observations were made with the help of E. Hilliard, a Masters student. No evidence was found for a spinodal decomposition in the Ti-25 wt.%Mo despite this treatment being located directly in the proposed phase field. However, further investigation is recommended and STEM-EDX, STEM-EELS and STEM-HAADF observations could be made to confirm this. Severe composition segregation was found in the Ti-45 wt.%Mo and Ti-60 wt.%Mo alloys. However, the same segregation was found in the as-cast SEM images. Therefore, it was concluded that 500 hours was not sufficient to homogenise this large quantity of Mo which means a further thermal treatment should be conducted in further work to reduce cast segregation. Following these investigations, the absence of a monoeutectoid reaction in Ti-Mo can be supported.
8.2 The nature of isothermal, equilibrium, stress-induced and trigonal $\omega$

The ADF-STEM imaging approach of taking images at several collection angles, which was used to investigate the observed tri-layer periodicity in $\beta$-Ti alloys, could be utilised in the further study of $\omega$ precipitates. Critically, the collection angle with which a tri-layer periodicity switch occurs was shown to be dependent on the extent of collapse of the $\{111\}_\beta$ towards the ideal $\omega$ structure. Therefore, it is suggested that this method is used to investigate the nature of isothermal, equilibrium, stress-induced and trigonal $\omega$.

It is proposed that the isothermal $\omega$ within Figure 7.1c should be studied first using STEM-HAADF techniques. Following HAADF imaging, the inner collection angle should be varied to determine the amount of coherency breaking on the collapsing $\{111\}_\beta$. It may be more difficult to observe the tri-layer periodicity in regions containing large isothermal $\omega$ precipitates because the multi-slice simulations, conducted as part of this project, have shown that single phase atom columns will not contain any tri-layer periodicity. Therefore, thicker regions of material may need to be investigated in order to contain $\beta + \omega$ through the thickness. This means better probe aberration corrections may be required to detect structural characteristics. The total scattering results in Chapter 6 provided evidence that isothermal $\omega$ contains an ideal $\omega$ structure rather than partial $\{111\}_\beta$ collapse. As a result of this, it would be expected that any tri-layer periodicity would switch at a different inner collection angle when compared to the athermal $\omega$ case reported in Chapter 4.

If the structure of isothermal $\omega$ can be quantified using the ADF method, it may be advantageous to compare this non-equilibrium isothermal phase with the true equilibrium $\omega$ counterpart. At room temperature and pressure, the $\omega$ phase is a metastable and non-equilibrium phase. Despite this, Chapter 3 did show that the non-equilibrium phases persisted over 500 hour heat treatments. In contrast, equilibrium $\omega$ is stable at high pressures. Therefore, by imaging with different inner collection angles, it would be interesting to compare the structure of the persistent isothermal $\omega$ phase to the equilibrium high pressure counterpart. A similarity in structure between the two may elucidate why isothermal $\omega$ is present following long thermal treatments.

The formation of equilibrium $\omega$ is expected to be difficult. In an attempt to manufacture equilibrium $\omega$, an offline high pressure experiment was performed at ISIS using a Paris-Edinburgh cell with the assistance of Dr. M.Tucker. Pressure was applied using toroidal
tungsten carbide anvils in a manner similar to that used by Bull et al. [217]. Samples of Ti-15 wt.% Mo in the $\beta$ quenched condition were pressurised to 800 and 1000 bar within a 30 minute period, pressure soaked for 75 minutes and then depressurised at a rate of 10-20 bar/min. Diffraction data from the 800 and 1000 bar samples are shown in Figure 8.1 and are compared to the quenched and unpressurised condition. Samples which were pressurised contained the same number of peaks when compared with the unpressurised sample. This could suggest a reversible transformation had occurred following depressurisation. Consequently, an in situ pressure experiment was also conducted on the Polaris beam line. In this experiment, neutron diffraction patterns were acquired whilst the material was pressurised to 1000 bar. It was found that the diffraction patterns from the in situ experiment contained more diffraction peaks due to the presence of the Paris-Edinburgh cell in the beam. Despite the additional peaks, there was no clear evidence for additional phases at 1000 bar. Therefore, the tungsten carbide anvils used in this experiment may not have been sufficient to enter the equilibrium $\omega$ phase field at room temperature. A higher pressure experiment using diamond anvils is suggested in future attempts to manufacture equilibrium $\omega$.

Interestingly, optical microscope images of the buckled cylinders following the pressurisation attempts showed lath-like features similar to those reported in Chapter 5. These can be deduced as large $\beta$ twins from their appearance and may contain stress-induced $\omega$ or $\omega$ on the $\beta$ twin boundaries. Therefore, the nature of these $\omega$ phases could also be investigated using HR STEM ADF imaging at different inner collection angles. It is suggested that the deformed samples should be surveyed for regions of interest, with material removed from several twins interfaces by FIB techniques. If this method is successful, it follows that the same $\omega$ investigations could be made from interrupted tensile tests that may deform by a martensitic transformation.

Finally, the nature of the athermal, isothermal, equilibrium and stress-induced $\omega$ could be compared to alloys containing a higher quantity of Mo. For example, alloys of Ti-20 wt.% Mo, Ti-30 wt.% Mo and Ti-40 wt.% Mo may provide interesting studies. It is thought that the structure of $\omega$ in more stabilised Ti-Mo alloys tends towards a trigonal unit cell rather than hexagonal one [7]. Using the ADF technique developed in this work, the premise of this can be explored with greater confidence.
Fig. 8.1 Neutron diffraction data from the 90° bank of Polaris, ISIS. Traces of atmospheric pressure, 800 Bar and 1000 Bar are shown. The dominant $\beta$ peaks have been labelled.
8.3 Artefacts

Chapter 5 provided evidence that thin foil analysis may not represent bulk material. In particular, a thinning induced transformation and an ordering transformation were observed. It was hypothesised that both of these transformations may have been influenced by a local increase in hydrogen. Therefore, further work is required to investigate the level of hydrogen in foils prepared using different methods. For example, the amount of hydrogen uptake could be measured for different electropolishing parameters such as: voltage, solution type, concentration, time and jet force. Furthermore, focused ion beam milling of foils using gallium ions may be improved using different procedures, for example, optimising current, number of steps and tilt [183]. In particular, gentle He-FIBing may be beneficial, although the additional expense might not be justified.

8.4 Total scattering

It was shown in Chapter 6 that total scattering analysis is a powerful experimental tool for investigating local structure in metastable $\beta$ alloys. Total scattering results were only shown up to the creation of the pair distribution function (PDF). In particular, an understanding of the system was extrapolated by comparing the experimental PDF trace to simulated PDF traces of: perfect $\beta$, ideal $\omega$, combinations of perfect $\beta$ with ideal $\omega$ and a frozen phonon description (Figure 6.10). These simulated PDF traces were constructed from a superstructure of 4000 atoms, of which 15 wt.% were Mo atoms randomly distributed. These atoms are fundamentally not the same as they contain different atomic masses and numbers. Therefore, it is unlikely that the two species are truly randomly distributed in any given lattice. Evidence for dissimilar bonding (Ti-Mo) in the $\beta$ phase was found within Chapter 5. Following heating of a thin foil to 300$^\circ$C, an ordered B2 structure was discovered. In this case, the body centre position at 1/2,1/2,1/2 contained a different species to the 0,0,0 position. Therefore, given the release of constraints associated with a thin foil, Ti-Mo bonding was preferred. Critically, further information about Mo site preference in the $\beta$ and $\omega$ structures could be extracted from total scattering data by employing a reverse Monte-Carlo approach using the newly developed RMCPProfile software. Unfortunately, RMCPProfile software is currently limited to determining local occupancies in single phase systems. However, this limitation was partially overcome by building simulations of a trigonal system and varying the \{111\}_$\beta$ collapse to either fit the $\beta$ or $\omega$ phases. Whilst these fits were found to be unstable, it is suggested that this method of analysis should be explored further as the following preliminary investigations
were found to be successful.

In the Monte-Carlo approach, 4000 atoms were minutely shifted and swapped within the three different starting structures mentioned above. With each atom change, the fit was compared between the simulated and experimental PDF results. The fit was further refined by acceptance of the shift or swap if there was a least squares improvement. Furthermore, the experimental structure factor and Bragg data could also be included in this refinement, such that only atom shifts or swaps that improved the Bragg, structure factor and PDF fits were accepted. This meant that subtle long range and short range features could be extracted from the experimental data by looking at the refined model structure. Using the trigonal approach, some reasonable fits were achieved. Example reverse Monte-Carlo fits to PDF and Bragg data for the as-sprayed Ti-15 wt.%Mo powder are shown in Figure 8.2. The lines show the calculated PDF and Bragg fits as determined using RMCProfile fitting to a trigonal structure, the circles show the experimental X-ray data. It can be seen in Figure 8.2 that the $\beta$ and $\omega$ structures can be reproduced despite the technique’s limitation to one phase. However, it was found that the two phase treatment made the RMCProfile fitting sensitive to fitting parameters such as the weighting between the PDF data, structure factor data and Bragg data. Figure 8.2a-b are PDF and Bragg fits following weighting towards the PDF data. Figure 8.2c-d are PDF and Bragg fits following weighting towards the Bragg data. The residual between fit and experiment was found to vary dependent on the weighting. This meant that the resultant structures following fitting were different, giving different solutions. Therefore, further study of the fitting parameters is recommended before conclusions can be drawn.

The anticipated approach following RMCProfile fitting is to collapse the refined superstructure of atoms onto a single unit cell to determine the average positions of each species. Figure 8.3 is the collapsed structure from a solution found in Figure 8.2a-b. It can be seen that the frozen phonon is described by the continuum between the $\beta$ and $\omega$ positions. Interestingly, this particular solution showed that the Mo atoms were not involved in the $\{111\}_\beta$ collapse which may be a significant result and be cause for further refinement of fitting parameters.

Reasonable Monte-Carlo fits for in situ data of material heat treated at 30, 100, 200, 300 and 400°C are also shown in the Appendix (Figures A.1, A.2, A.3 and A.4). Uniquely, the RMCProfile deduced superstructure was then taken and run through electron-multislice simulation software to simulate the HAADF atom column appearance along zones of interest. Some preliminary results (Figure 8.4) showed the rejection of Mo atoms from $\omega$ sized regions as the temperature was increased from 30 to 400°C. It can be seen that this method of analysis
Fig. 8.2 Results of RMCPProfile fitting (black line) to experimental data (circles). a-b) PDF and Bragg fits following weighting towards the PDF data. c-d) PDF and Bragg fits following weighting towards the Bragg data. The residuals lines are plotted on parts a & c below the fitted model. The residual between fit and experiment was found to vary dependent on the weighting. Therefore, the resultant structures following fitting were different.
Further Work

Fig. 8.3 A single unitcell of the RMCPProfile refined structure shown along <110>β. The unit cell contains all the positions of the Ti atoms (black) and Mo atoms (red) that were present in the supercell. The blue line shows the diagonal.

is potentially very useful because it links the HAADF experimental observations directly to the total scattering observations. For further study, a data analysis strategy is suggested. This strategy is outlined in Figure 8.5 and is an iterative approach between experimental data and simulations using the methods developed in this thesis. It is hoped that by improving the simulations, nature of β titanium alloys can be understood in more detail.

The downside of employing the strategy in Figure 8.5 for further work is the cost and time required for the techniques involved. However, the more data that is collected, the stronger the case can be made. A major advantage of the RMCPProfile fitting to total scattering data is that multiple experiments can be analysed concurrently. Consequently, preliminary neutron total scattering data was acquired for the as-sprayed Ti-15 wt.%Mo powder. Importantly, Ti has a negative neutron scattering cross section. Therefore, the Ti-Mo bond has a negative scatter rather than a positive one. In contrast, both Ti-Ti and Mo-Mo bonds scatter neutrons in the positive direction and all bonds scatter in the positive direction for X-rays. The PDF trace from X-ray and neutron data is shown in Figure 8.6. The PDF traces, G(r), are weighted sums of the partial g(r)’s. Due to the difference in the g_{Ti-Mo}(r) between X-rays and neutrons, the G(r) traces are different. The advantage of this is more data can be extracted. For example, by examination of the distance corresponding to 4.8 Å (which is close to the ω lattice parameter),
Fig. 8.4 ADF muti-slice simulations of RMCPProfile deduced superstructures which were fitted against total scattering data acquired at 30, 200, 300 and 400°C. Bright atom columns contain an increased quantity of Mo atoms.
Fig. 8.5 A strategy to improve the understanding of the nature of $\beta$ titanium alloys. The cycle utilises experimental and simulation data which could help refine the understanding of phases such as the $\omega$ phase.
Fig. 8.6 PDF graphs of Ti-15wt.%Mo powder in the as-sprayed condition. The red trace was determined from X-ray data and the green from neutron scattering data. The insert schematic is to show how the $G(r)$ peak at 4.8 Å is a weighted average of the partial $g(r)$'s for Ti-Ti, Mo-Mo and Ti-Mo. By examining the peak shapes at 4.8 Å, it was deduced that the Ti-Mo bond length is less disordered than Ti-Ti and Ti-Mo.

it was deduced that the Ti-Mo bond is less positionally disordered than the Ti-Ti and Ti-Mo bonds. This observation was made solely on the shapes of the PDF peaks at 4.8 Å. The insert schematic in Figure 8.6 represents how the $G(r)$ peaks could be constructed from the partial $g(r)$ peaks for both X-rays and neutrons. It was found that the two experimental peaks at 4.8 Å could only be reproduced if the Ti-Mo peak was narrower than the Ti-Ti and Mo-Mo peaks. This effectively suggests Mo atoms are less likely to be on the collapsing $\{111\}_{\beta}$. This observation correlates with Figure 8.3 but further work involving full pattern reverse Monte-Carlo fitting using both the neutron and X-ray data is needed.

In general, significant progress was made during this project in the application of the total scattering technique to $\beta$ titanium alloys. However, applying total scattering techniques to engineering metals is still under development. As such, there are still barriers which need to be overcome in further work before the results can be deemed accurate enough to represent reality. Ultimately, many RMC profile fits would need to be made against experimental data.
acquired in different ways, with each fit containing different numbers of atoms and starting conditions. The solution will only be found if each fit converges to the same atom distribution and sufficiently matches the experimental results. This degree of convergence was not found in this work. Within this work several parameters were highlighted that disrupted convergence and affected the results. It was found that the effects of: detector clipping, data truncation, data weighting, texture and phonons all require further study. Fundamentally, however, more control of the fitted structure is required within RMCProfile.

8.5 Modelling

Local occupancy in Ti-15 wt.%Mo remains an intriguing question that could be investigated using modelling techniques. One advantage of modelling would be to add validity to the proposed structures created from RMCProfile fits of total scattering data. Two superstructure ab initio modelling methods were prescreened to investigate Mo atom site preference, both using CASTEP density functional theory (DFT) software. The first method considered the free energy of a series of $\beta$ unit cells (also known as a supercell) as a function of the separation of Mo atoms within the supercell. The second method investigated the energy of a series of perfect $\beta$ supercells as the structure transformed into a series of idea $\omega$ unit cells. Furthermore, the separation and concentration of the Mo atoms was varied to examine the effects on activation energy during this transformation.

The first method involved calculations to examine the interaction energy between two Mo atoms which substitutionally sit on the $\beta$ Im-3m supercell. The aim was to plot the change in supercell energy as function of Mo separation and temperature. Although DFT can easily include the effects of pressure and becomes more accurate with increasing pressure, the effects of temperature are harder to include. One idea was to assume the temperature effects on the free energy are more dominant than phonon interactions, as used by Benes et al. [218]. Therefore, DFT calculations could be used to estimate the partition function, $Z$, and as a result Helmholtz free energy, $\Omega$, as a function of temperature through Equations 8.1 and 8.2.

$$Z = \sum_r \exp \left( -\frac{\phi(r)}{k_BT} \right) \quad (8.1)$$

$$\Omega = -k_BT \ln Z \quad (8.2)$$
Where the partition function, $Z$, is dependent on the excess configurational energy, $\phi$, which varies with Mo pair separation, $r$. $k_B$ is Boltzmann constant and $T$ is the temperature. Using Equation 8.3, the probability of finding a Mo configuration, $p(r)$, can be plotted as a function of temperature.

$$p(r) = \frac{g(r) \exp\left(\frac{-\phi(r)}{k_B T}\right)}{Z} \quad (8.3)$$

Where $g(r)$ is the number of ways two Mo atoms can be arranged in a supercell with separation $r$. Note that these treatments only work for constant volume. For this reason, a geometry optimisation was conducted for a supercell of $2 \times 2 \times 2$ of Im-3m unit cells with only Ti atoms. The resulting lattice parameters, which correspond to the lowest ground state energy for pure Ti, were then fixed for subsequent calculations. One advantage of not having to do a geometry optimisation for each energy calculation is that it reduces computation time from weeks to days per calculation. However, full geometry optimisation would need to be conducted in further work. The lattice parameters used were $a=b=c=3.267$ Å. Using these lattice parameters the variation of ground state energy is shown for different sized supercells in Table 8.1.

<table>
<thead>
<tr>
<th>Size of superlattice</th>
<th>Ground state energy for pure Ti superlattice</th>
<th>Energy per atom</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1 \times 1 \times 1$</td>
<td>-3205.246</td>
<td>-1602.623</td>
</tr>
<tr>
<td>$2 \times 2 \times 2$</td>
<td>-25642.017</td>
<td>-1602.626</td>
</tr>
<tr>
<td>$3 \times 3 \times 3$</td>
<td>-86541.800</td>
<td>-1602.625</td>
</tr>
</tbody>
</table>

Table 8.1 Ground state energy for pure Ti calculated using superlattices with the Im-3m structure. For the $2 \times 2 \times 2$ superlattice, geometry optimisation was used. For the other two, single point calculations were conducted using the parameters as determined in the geometry optimisation.

A simple way of evaluating the interaction energy was to calculate the binding energy between a pair of Mo atoms as a function of their separation. The binding energy calculation used was that used by Mottura et al. [219] and shown in Equation 8.4, with a negative value being an attractive arrangement and a positive being a repulsive one.

$$E_{\text{Bind}}(\text{Mo} - \text{Mo}) = 2E(\text{Ti}_{N-1}\text{Mo}_1) - E(\text{Ti}_{N-2}\text{Mo}_2) - E(\text{Ti}_N) \quad (8.4)$$
Further Work

Fig. 8.7 Binding energy between two Mo atoms as a function of their separation. Negative values indicate attractive. Number of atoms, \( N \), is 16 and 54 for the \( 2 \times 2 \times 2 \) and \( 3 \times 3 \times 3 \) respectively.

Where \( E_{\text{Bind}}(\text{Mo} - \text{Mo}) \) is the binding energy between two Mo atoms, \( E(\text{Ti}_{N-1}\text{Mo}_1) \) is the energy of a supercell of \( N \) atoms with 1 Mo atom, \( E(\text{Ti}_{N-2}\text{Mo}_2) \) is the energy of a supercell of \( N \) atoms with 2 Mo atoms, and \( E(\text{Ti}_N) \) is the energy of a pure Ti supercell.

Preliminary calculations were performed for a \( 2 \times 2 \times 2 \) supercell (16 atoms) and a \( 3 \times 3 \times 3 \) supercell (54 atoms). The atoms were not placed on faces, edges or corners of the supercell in order to suppress edge effects and the treatment ignored the interaction of the Mo atoms in neighbouring superlattices. As a result, there is considerable disagreement between the \( 2 \times 2 \times 2 \) superlattice and \( 3 \times 3 \times 3 \) supercell, especially at about 5.5Å where the signs are different, see Figure 8.7. Additionally, despite increasing the separation in the \( 3 \times 3 \times 3 \) cell, the binding energy appears to have some periodicity. This is due to the fact that as Mo atoms get further apart in the supercell, they become closer to other Mo atoms in neighbouring supercells. To this end, calculated values at 3.23, 4.48 and 5.49Å are the same as 6.33, 10.97 and 7.08Å. Therefore, the radial distribution function of the Mo atoms has to be taken into consideration.

For each Mo pair separation, the radial distribution of Mo atoms was determined to a distance of 20Å. Using all the calculations across several sized supercells, a set of simultaneous equa-
tions were established with the form in Equation 8.5, where (A) is the CASTEP calculated ground state values and (B) is the number of bonds for separation with energy (C).

\[(A) = (B)(C)\]  

(8.5)

Using Microsoft Excel 2010’s least squares solver tool, model parameters were optimised to reduce the square of the difference between a Gaussian based model and the calculated results. In the model, the energy due to the Mo and Ti atoms was also included as a parameter, so the resulting energies are the excess energies due to having two Mo atoms at that separation; the excess configurational energy. The model was built with the help of Dr G. Conduit from the Physics group in the Cavendish Laboratory, Cambridge University. The excess configurational energy was plotted as a function of Mo pair separation and shown in Figure 8.8. The shape of Figure 8.8 tracks the shape of the $3 \times 3 \times 3$ supercell, which suggests a larger supercell was more accurate.

Using Equations 8.1 and 8.3, the normalised probability change with temperature can be plotted and is shown in Figure 8.9. Figure 8.9 shows an increased probability of finding neighbouring Mo atoms as the temperature is reduced. Therefore, at high temperatures, the energy of the system could be reduced with a higher proportion of Ti-Mo bonding. This agrees with the experimental observations, reported in Chapter 5, that a B2 formed on heating to 300°C rather than on cooling to cryogenic temperatures.

The second method used in this project to investigate site preference was to simulate the phase $\beta$ to $\omega$ athermal transformation. Since the relation between $\beta$ and $\omega$ is known, the BCC structure was redefined to an equivalent unit cell with 3 atoms. A Transition State Search (TSS) was then used to investigate the energy change from $\beta$ to $\omega$. Specifically, the energy of the structure was calculated as the collapse of the {111} planes was simulated.

Some preliminary Transition State Search (TSS) calculations were conducted. The reaction pathway defined was perfect $\beta \rightarrow$ ideal $\omega$. A $2 \times 2 \times 2$ supercell was used and this supercell contained 24 atoms. Two of the atoms were Mo atoms, giving a simulated atomic composition of 8.3%, which is very close to Ti-15 wt.%Mo. The TSS was done for: 1) Mo shared across collapsing and stationary positions, 2) Mo atoms on the corners and Ti atoms collapsing, and 3) Ti on the corners with one Mo and one Ti collapsing. For each condition, the calculations were re-run for all possible combinations of Mo separations. The resultant energies were each normalised against the start energy and are shown in Figure 8.10. The
Fig. 8.8 Excess configurational energy as a function of Mo pair separation. The Mo pair separations are linked with a dotted line as each separation does not have the same extent of screening.

Fig. 8.9 The change in probability of finding a pair of Mo atoms as a function of their separation and temperature.
preliminary results showed that the energy change associated with Mo separation was much smaller than the energy change as the structure transformed. Specifically, the energy change on the vertical axis was smaller than the change on the horizontal axis. Interestingly, the results suggest that $\omega$ is more stable than $\beta$. This is not backed up by the experimental results and emphasises the limitations of *ab initio* modelling. For example, only the outer electrons were considered, and different results may be found using a different number of electrons or by changing other parameters in the calculations such as sampling density.

Despite the limitations in DFT discussed here, TSS is still worth further investigation. Primarily this is because of the activation energies found within Figure 8.10. Critically, the local occupancy of the Mo atoms changed the height of the energy barrier between the $\beta$ and $\omega$ phases. It was found that when Mo atoms were located on the collapsing $\{111\}_\beta$ planes, the activation energy was lower. Interestingly, this is effectively opposite to the initial assumption made that Mo sits on the stationary un-collapsing planes resulting in tri-layer periodicity. With further investigation, DFT may be a very powerful tool for understanding transformations in metastable $\beta$ alloys that contain multiple components.
Fig. 8.10 The energy change during the \{111\}_\beta plane collapse for different configurations of Mo atoms and for Mo atoms at different separations.
This project has shown that the nature of the $\omega$ phase can be characterised and the experimental evidence reported here is sufficient to have confidence in the results. In addition, the extension of the techniques used during the project to high temperature *in situ* settings has been found to be only limited by oxidation and stability concerns. Once these limitations are overcome, the next step would be to repeat the investigations of the $\omega$ phase at temperatures within the $\beta$ phase field, and thereby isolate the effect of the $\beta$ quench. Furthermore, the role of the $\omega$ phase in $\alpha$ phase nucleation is still an intriguing area of contention that may be explored further using the techniques described in this work. Only through developing a full understanding of the $\omega$ phase can this avenue for strengthening in metastable $\beta$ titanium alloys be fully exploited. Therefore, it is envisioned that techniques investigated and developed within this thesis will be critical to future alloy development and research.
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Appendix A
Fig. A.1 RMCProfile reverse Monte-Carlo fits (red line) against experimental data from Ti-15wt.%Mo (black line) acquired at 30°C. a) Bragg fit, b) S(Q) fit, c) PDF T(r) fit (this is a re-weighted G(r) to suppress phonon dampening effects) and d) partial g(r) fits for Ti-Ti (black), Ti-Mo (red) and Mo-Mo (green). Fit stopped following 340046 atom moves generated, 304075 moves tried and 8851 moves accepted.
Fig. A.2 RMCProfile reverse Monte-Carlo fits (red line) against experimental data from Ti-15wt.%Mo (black line) acquired at 200°C. a) Bragg fit, b) S(Q) fit, c) PDF T(r) fit (this is a re-weighted G(r) to suppress phonon dampening effects) and d) partial g(r) fits for Ti-Ti (black), Ti-Mo (red) and Mo-Mo (green). Fit stopped following 704845 atom moves generated, 656864 moves tried and 12584 moves accepted.
Fig. A.3 RMCProfile reverse Monte-Carlo fits (red line) against experimental data from Ti-15wt.%Mo (black line) acquired at 300°C. a) Bragg fit, b) S(Q) fit, c) PDF T(r) fit (this is a re-weighted G(r) to suppress phonon dampening effects) and d) partial g(r) fits for Ti-Ti (black), Ti-Mo (red) and Mo-Mo (green). Fit stopped following 286737 atom moves generated, 279258 moves tried and 6939 moves accepted.
Fig. A.4 RMCPROFILE reverse Monte-Carlo fits (red line) against experimental data from Ti-15wt.%Mo (black line) acquired at 400°C. a) Bragg fit, b) S(Q) fit, c) PDF T(r) fit (this is a re-weighted G(r) to suppress phonon dampening effects) and d) partial g(r) fits for Ti-Ti (black), Ti-Mo (red) and Mo-Mo (green). Fit stopped following 346839 atom moves generated, 303547 moves tried and 10638 moves accepted.