PHASE TRANSFORMATIONS IN THE CENTRAL PORTION
OF THE Nb-Ti-Al TERNARY SYSTEM

By

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Abstract of Dissertation Presented to the Graduate School of the University of Florida in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

PHASE TRANSFORMATIONS IN THE CENTRAL PORTION OF THE Nb-Ti-Al TERNARY SYSTEM

By

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Chairperson: Dr. Fereshteh Ebrahimi
Major Department: Materials Science and Engineering

Intermetallics in the Nb-Ti-Al ternary system have been considered for high temperature aerospace applications, and their development requires a thorough understanding of phase equilibria and phase transformations. In this study, transmission electron microscopy (TEM) was primarily used to investigate the phase equilibria and phase transformations of two alloys with compositions of 27Nb-33Ti-40Al (alloy 2) and 42Nb-28Ti-30Al (alloy 4). Small arc melted samples were thermally aged at temperatures between 400°C and 1550°C for four to sixteen hours (long-term), and at 1000°C and 1200°C for two to five minutes (short-term), followed by either water quenching, air cooling, or furnace cooling.

The equilibrium phase study showed that both alloys solidified as the β phase, which becomes ordered to the B2 phase during solid state cooling. The σ-Nb₂Al phase precipitated from the β phase slightly below 1400°C in alloy 2 and 1550°C in alloy 4. The σ phase formed as isolated grains above ≈1300°C in both alloys. Colonies of σ grains formed below ≈1300°C in alloy 4. A eutectoid transformation from β to σ + γ-
TiAl occurred at 1200°C in alloy 2. A discontinuous transformation from B2 to $\sigma + \beta$ occurred at 1000°C in alloy 4.

A metastable $\omega$-D phase formed by the collapse of $\{111\}_\beta$ planes and chemical ordering from the B2 phase in alloy 2 during slow cooling. The $\omega$-D phase consisted of the Al$_4$Ti$_3$Nb$_2$ stoichiometry and P6$_3$/mcm space group. A proposed model showed aluminum and niobium on single layers, and titanium and aluminum on double layers. The transformation path was described using subgroup and symmetry relations as: Pm$\overline{3}$m(B2) $\rightarrow$ P$\overline{3}$1m($\omega''$) $\rightarrow$ P6$_3$/mcm(\omega-D).

A martensitic transformation of the $\beta$ phase to plates occurred during fast cooling in alloy 2. The observed habit plane of the plates agreed with that calculated using the invariant line theory. The $\beta$ composition affected the formation of structurally related orthorhombic (Pmma and Cmcm) and HCP (P6$_3$/mmc) plates. The proposed site occupancy showed the Al$_4$TiNb stoichiometry for the Cmcm phase.

Analysis of domain structures, stacking faults, and electron diffraction suggested two possible transformation paths: Im$\overline{3}$m($\beta$) $\rightarrow$ Cmcm(disordered) $\rightarrow$ P6$_3$/mmc(disordered) $\rightarrow$ P6$_3$/mmc(D0$_{19}$) for HCP plates and Pm$\overline{3}$m(B2) $\rightarrow$ Pmma $\rightarrow$ Cmcm(ordered) for orthorhombic plates.
CHAPTER 1
INTRODUCTION

The ternary Nb-Ti-Al system is recognized as a technologically important system. Alloys based on this system have found many applications, especially in the aerospace industry. The titanium-based alloys have long been studied and used in aeronautical applications because of their low densities and high strengths [1,2]. There is currently the need for higher temperature and higher strength materials to improve the performance of gas turbine engines and structural airframe components of modern aircraft. This will require different materials than the current nickel-based superalloys and conventional titanium-based alloys. The nickel-based alloys are heavy and have reached practical limits imposed by operating temperatures that are ≈85% of their melting point [3,4]. The titanium-based alloys do not possess sufficient mechanical properties, such as creep and oxidation resistance, at high temperatures [5]. Thus, the current need to improve the properties of these materials has led to the development of intermetallic titanium-aluminides [5-8]. Additions of niobium to these titanium-aluminides make these alloys even more attractive by improving the mechanical properties. However, the materials needed for the next generation of high performance gas turbine engines, etc. still need further improvements in lower density, better mechanical properties, and higher operating temperatures. To meet these needs, research is being conducted on refractory-based alloys, ceramics, composites, and intermetallics.
Ordered intermetallic compounds based on refractory metals such as niobium have been identified as potential materials that may meet the high-temperature requirements of advanced turbine engines [9]. The attractive properties of refractory-based intermetallics include combinations of high melting temperature, lower density, high stiffness, and good creep/strength resistance. However, monolithic ordered intermetallics typically show poor mechanical properties at low temperatures, of which the low fracture toughness is the most serious problem. The current trend to overcome these problems has been through the use of composites and alloy development based on two-phase and multi-phase systems incorporating Nb-based intermetallics and ductile second phases. The Nb-Ti-Al system shows potential phase relationships between the intermetallic $\sigma$-Nb$_2$Al phase, which has a high melting point of 2060°C; the BCC $\beta$ or B2 phases, which have extensive ternary composition ranges; and other technologically important intermetallics, such as the $\alpha'$-Ti$_3$Al, $\gamma$-TiAl, O-Ti$_2$NbAl, and $\eta$-(Ti-Nb)Al$_3$ phases [10-13]. Thus, the development of these alloys for the improvement of properties requires a thorough understanding of the phase relationships in this system.

There have been a number of studies over the past thirty years that have contributed to the current understanding of the phase equilibria and phase transformations in the Nb-Ti-Al system. However, a thorough understanding of these topics is far from being complete. The reason for this lack of understanding can be attributed to the complex phase relationships arising from a multitude of equilibrium and metastable phases in this ternary system. In addition, the solidus temperature over a large portion of this ternary system lies above \( \approx 1500°C \). The high solidus temperature limits the practical number of isotherms that can be developed in
systematic studies using large numbers of alloys with different compositions. Thus, the systematic studies in the past have concentrated on determining the phase equilibria at just one or two temperatures, with the most common temperature at 1200°C. Surprisingly, the phase equilibria and phase transformations in the central portion of this system have not been investigated very thoroughly in the past. This central portion contains ternary solubility extensions of the binary $\sigma$-Nb$_2$Al and $\gamma$-TiAl phases and the ternary $\beta$/B2 phases, which have attractive properties such as high melting point, low density, and reasonable oxidation resistance. Therefore, it was the purpose of this study to provide basic research on the phase relationships in the central portion of the ternary Nb-Ti-Al system.

A review of previous literature on the phase equilibria in the ternary Nb-Ti-Al system is given in Chapter 2. From this literature survey and preliminary experimental results, two alloys were selected based on two-phase microstructures that contained the $\sigma$ phase and either the B2 or $\gamma$ phases. A third alloy was also investigated in order to study the influence of aluminum on the ordering in the $\beta$ phase to the B2 phase that has been shown to occur in this ternary system. Both long term and short term heat treatments at high temperatures were employed to study the high temperature phase equilibria and their evolution. The stability aspect of the $\beta$ phase with regard to metastable phase formations was investigated using different cooling rates in the high temperature heat treatments. Transmission electron microscopy (TEM), utilizing the imaging, selected area electron diffraction (SAED), and convergent beam electron diffraction (CBED) capabilities, was selected as the primary analytical technique to identify and study the phases. The details
concerning the alloy compositions, heat treatments, analytical techniques, and specimen preparation are presented in Chapter 3.

Since the central portion of this ternary system is complicated, an analysis of the results of the equilibrium phases are presented in Chapter 4. The equilibrium phases present at high temperatures and the formation of these phases are described from the analysis of the long term and short term heat treatments. The influence of cooling rate on the formation of metastable phases from the high temperature β phase is also introduced in this chapter. Following the analysis of the equilibrium phases, detailed studies of the metastable phase formations are presented in Chapters 5 and 6.

Chapter 5 covers the metastable ω-related phase that forms from the β phase in alloy 2. The analysis of the structure and the effects of composition, cooling rate, and low temperature heat treatments are covered in this chapter. From these results, the proposed atomic site occupancy of this ω-related phase and a description of the β to ω phase transformation using subgroup and symmetry relations is given.

Chapter 6 analyzes the metastable plates that formed from the β phase in alloy 2. The analysis of the crystal structures and defect structures of these plates is covered. The influence of the heat treatment and β composition on the structure and formation of the plates is analyzed. The transformation of the β phase to plates is shown to be consistent with martensitic transformations using the invariant line theory. Finally, the structure of the plates is described using subgroup and symmetry relations to show that two different transition paths lead to different plate structures.
CHAPTER 2
LITERATURE SURVEY

In this chapter, an overview of the published literature on the phase equilibria and phase transformations in the ternary Nb-Ti-Al system is presented. Due to the complexity of this system, this overview will focus only on those phases that were observed in the alloys investigated in this study. Therefore, this chapter is divided into six sections: the ternary phase equilibria studies, the sigma (σ) phase, the gamma (γ) phase, the B2 phase, the omega (ω) phase, and the ortho(hex) phases. The orth(hex) designation is used in conjunction with the two closely related orthorhombic and hexagonal close packed (HCP) structures. The first section on the ternary phase equilibria studies describes the various developments in the overall ternary phase diagram. This section is divided into two subsections based on the results from the survey studies and the Ti-based alloy development studies. The remaining sections on the σ, γ, B2, omega (ω), and orth(hex) phases describes the research pertinent to each of these specific phases. The sections dealing with the σ, γ, and B2 phases are relevant to the equilibrium phase study in Chapter 4; the ω phase is relevant to the ω-related phase transformation study in Chapter 5; and the orth(hex) phases are relevant to the plate transformation study in Chapter 6.

2.1 The Ternary Phase Equilibria Studies

The phase equilibria of the ternary Nb-Ti-Al system has been the subject of many investigations since the early 1950s. However, most of these studies can be
grouped into two main categories: those that surveyed the phase equilibria of alloys with compositions covering large regions of the ternary phase diagram at discrete temperature ranges, and those that concentrated in-depth on just a few compositions for the commercial development of Ti-based alloys over large temperature ranges. The survey studies investigated the phase equilibria of alloys at a limited number of temperatures, which was usually only one temperature and often 1200°C. The Ti-based alloy studies mostly focused on Ti-rich or Ti$_3$Al + Nb compositions with constant 25 at.% Al. The recent trend in the development of these Ti-based alloys has been in the ternary region between Ti$_3$Al and TiAl. These are binary phases with ternary additions such as Nb.

2.1.1 The Survey Studies

Most of the phases that have been observed in the ternary Nb-Ti-Al system are binary phases that showed large ternary solubility ranges. There have been many studies in the past that have determined the binary phases of the Nb-Ti, Nb-Al, and Ti-Al systems. These studies and the binary phase diagrams of the Nb-Ti, Nb-Al, and Ti-Al systems developed from them have been compiled in two main references [10, 11]. The results of these compiled studies have shown that there are at least ten equilibrium binary phases. A summary of the important information about these ten phases, such as the phase notation, the crystal structure, the point group, the reaction type, and the reaction temperature are shown in Table 2.1.

There currently exists some uncertainty concerning the phase equilibria in the Ti-Al phase diagram. This uncertainty is mainly between the $\gamma$-TiAl and $\eta$-TiAl$_3$ phases and is due to the formation of long-range periodic structures in this part of the binary system that can complicate the determination of the equilibrium phases.
Table 2.1. Information regarding the phases of the three binary Nb-Ti, Nb-Al, and Ti-Al phase diagrams [10,12].

<table>
<thead>
<tr>
<th>Phase Notation</th>
<th>Stoichiometry</th>
<th>Crystal Structure</th>
<th>Space Group</th>
<th>Reaction Type</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>β</td>
<td>Nb</td>
<td>BCC</td>
<td>Im3m</td>
<td>L ⇄ β</td>
<td>2467</td>
</tr>
<tr>
<td>α</td>
<td>Ti</td>
<td>HCP</td>
<td>P6₃/mmc</td>
<td>α ⇄ β</td>
<td>882</td>
</tr>
<tr>
<td>θ</td>
<td>Al</td>
<td>FCC</td>
<td>Fm3m</td>
<td>L ⇄ β</td>
<td>660</td>
</tr>
<tr>
<td>β₁</td>
<td>Nb₂Al</td>
<td>Cubic</td>
<td>Pm3n</td>
<td>L + β ⇄ β₁</td>
<td>2060</td>
</tr>
<tr>
<td>σ</td>
<td>Nb₂Al</td>
<td>Tetragonal</td>
<td>P4₃/mnm</td>
<td>L + β₁ ⇄ σ</td>
<td>1940</td>
</tr>
<tr>
<td>η</td>
<td>NbAl₃</td>
<td>BCT</td>
<td>I4/mmm</td>
<td>L ⇄ η</td>
<td>1680</td>
</tr>
<tr>
<td>α₂</td>
<td>Ti₃Al</td>
<td>HCP</td>
<td>P6₃/mmc</td>
<td>α ⇄ α₂</td>
<td>1180</td>
</tr>
<tr>
<td>γ</td>
<td>TiAl</td>
<td>Tetragonal</td>
<td>P4/mmm</td>
<td>L + α ⇄ γ</td>
<td>1450</td>
</tr>
<tr>
<td>δ</td>
<td>---</td>
<td>LPS</td>
<td>---</td>
<td>L + γ ⇄ β₁</td>
<td>1380</td>
</tr>
<tr>
<td>ε</td>
<td>TiAl₂</td>
<td>BCT</td>
<td>I₄/amd</td>
<td>γ + δ ⇄ ε</td>
<td>1240</td>
</tr>
<tr>
<td>η</td>
<td>TiAl₃</td>
<td>BCT</td>
<td>I₄/mmm</td>
<td>L + δ ⇄ η</td>
<td>1350</td>
</tr>
</tbody>
</table>

LPS is a long-period superlattice structure; β-Ti and β-Nb are isomorphous across the binary Nb-Ti phase diagram; and η-NbAl₃ and η-TiAl₃ are isomorphous across the ternary phase diagram for constant Al.
The binary Ti-Al phase diagram originally developed by Murray [10] has recently been modified on the Ti-rich side from the results by Valencia et al. [15] in 1987 and by McCullough et al. [16] in 1989. This modification involved the phase boundaries between the α-Ti and γ phases. It had previously been shown that the α-Ti phase formed from the peritectoid β + γ ↔ α reaction near \( \approx 1480°C \), but the results of these recent studies showed that the α-Ti phase formed from the peritectic \( L + \beta \leftrightarrow \alpha \) reaction. The previously accepted binary Ti-Al phase diagram and the revised part of the phase diagram are shown in Figure 2.1. The temperature of the peritectic \( L + \beta \leftrightarrow \alpha \) reaction was estimated to be \( \approx 1475°C \) from the study by McCullough et al. [16]. Further studies by McCullough et al. showed that the single α-Ti phase was present in the Ti-50at.%Al alloy at a temperature of \( \approx 1450°C \).

Therefore, the results of these two studies indicated that the α-Ti phase in binary Ti-Al alloys was stable at high temperatures and with compositions containing up to 50at.%Al.

One of the first survey studies of the phase equilibria in the ternary system was reported by Popov and Rabezova in 1962 [17]. In this study, the Nb rich side of the ternary phase diagram and the ternary solid solution range of the binary γ (TiAl) phase were examined. Isothermal sections were constructed at 1400°C, 1200°C, and room temperature from the phase analysis of the heat treated samples. The results of this study showed the existence of a ternary intermetallic compound that was given the notation of the γ₁ phase. The γ₁ phase was determined to have a tetragonal structure with a stoichiometric composition of NbTiAl₂ (at.%). The lattice parameters that were determined for the γ₁ phase were \( a = 3.56Å \) and \( c = 4.69Å \). It was also found that a quasi-binary section existed from NbAl₃ to Ti that contained the ternary
Figure 2.1. Shows the binary Ti-Al phase diagram. (a) the previously accepted [10] phase diagram; (b) the modified section of the phase diagram [5].
\( \gamma_1 \) phase. The NbAl\(_3\)-Ti quasi-binary section showed that the ternary \( \gamma_1 \) phase transformed congruently from the liquid phase at a temperature of \( \approx 1850^\circ \text{C} \). On opposite sides of the ternary \( \gamma_1 \) phase were the eutectic reactions of \( L \leftarrow \beta + \gamma_1 \) and \( L \leftarrow \gamma_1 + \eta \). The \( L \leftarrow \beta + \gamma_1 \) reaction occurred at \( \approx 1550^\circ \text{C} \), and the \( L \leftarrow \gamma_1 + \eta \) reaction occurred at \( \approx 1520^\circ \text{C} \). Although the precise boundaries of the phase equilibria were not reported, the results of this study indicated that extensive regions of ternary solid solutions existed for the binary \( \beta_1 \) (Nb\(_3\)Al), \( \sigma \) (Nb\(_2\)Al), \( \eta \) (NbAl\(_2\)), and \( \gamma \) (TiAl) phases.

In the following year, Wukusick [18] studied the ternary solid solution range of Nb in the \( \gamma \)-TiAl phase. The phase equilibria that were reported in this study were from X-ray diffraction analysis of alloys that were solution treated at 1425\(^\circ\)C and then water quenched. One of the alloy compositions that Wukusick investigated was 24Nb-26Ti-50Al (at.\%), which was close to the stoichiometric composition of the \( \gamma_1 \) phase (Nb\(_3\)TiAl\(_2\)). However, the results of this study did not support the results of Popov and Rabezova [17]. In this study, the \( \gamma \) phase, showing a large ternary solubility range for Nb, was observed instead of the \( \gamma_1 \) phase. Thus, the results by Wukusick contradicted the existence of the ternary \( \gamma_1 \) phase.

A study conducted by Zakharov et al. [19] in 1984 added to the confusion concerning the existence of the ternary \( \gamma_1 \) phase. This study examined the region of the ternary Nb-Ti-Al phase diagram where the two quasi-binary sections of NbAl\(_3\)-Ti and Ti\(_3\)Al-Nb intersected. The alloys investigated in this study were subjected to an extensive schedule of solutionizing heat treatments with final heat treatments at 1200\(^\circ\)C, 900\(^\circ\)C, and 600\(^\circ\)C for one hour and then water quenched. The phase equilibria of the aged samples were determined by X-ray diffraction. The most significant result of this study was the confirmation that the ternary \( \gamma_1 \) phase, which
was reported by Popov and Rebezova [17], existed with the stoichiometry of NbTiAl$_2$.
The study by Zakharov et al. also reported that the $\gamma_1$ phase had a tetragonal
structure. However, the lattice parameters that were reported for the $\gamma_1$ phase by
Zakharov et al. were different from those that were reported by Popov and Rabezova.
The lattice parameters reported by Zakharov et al. were $a = 8.418$ Å and $c = 4.538$ Å,
while the lattice parameters reported by Popov and Rabezova were $a = 3.56$ Å and $c = 4.69$ Å. The reason for the disagreement between the lattice parameters was not
known.

Two comprehensive studies that were published in 1989 by Jewett et al. [20] and
Kaltenbach et al. [21] investigated the phase equilibria of alloys that had
compositions covering the central portion of the ternary phase diagram. The study by
Jewett et al. examined fourteen different alloy compositions formed by heat treating
arc-melted samples at 1200°C for up to seven to sixteen days. In a similar manner,
Kaltenbach et al. examined thirty five different alloy compositions that were heat
treated at 1200°C for one to seven days. In general, there was good agreement
between the results of these two studies. Both studies indicated that the $\beta$ phase
existed at 1200°C over a substantial part of the ternary phase diagram. The binary
phases were observed to project into the ternary section with large solubility ranges
that loosely followed constant Al compositions. This projection can be seen by the $\beta_1$
(shown as $\delta$) and $\sigma$ phases on the binary Nb-Al side and by the $\gamma$ and $\alpha$ phases on the
binary Ti-Al side of the ternary isotherm shown in Figure 2.2. The $\eta$ phase was
determined to be isomorphous between the NbAl$_3$ and TiAl$_3$ phases, and was shown to
connect these two phases along the constant 75at.%Al composition line.
Figure 2.2. Shows the 1200°C isothermal section of the ternary Nb-Ti-Al system determined by Jewett et al. [20].
These results from the studies by Jewett et al. and Kaltenbach et al. helped to clarify the earlier results, but they also caused future problems concerning the phase equilibria in the Nb-Ti-Al system. Both of these studies concluded that the ternary $\gamma_1$ phase did not exist in this system. It was found instead that alloys with compositions close to that reported for the $\gamma_1$ phase consisted of the binary $\gamma$-TiAl phase. These studies also showed that the $\gamma$ phase had a substantial solubility limit for Nb. Jewett et al. reported a solubility of up to 30at.\%Nb in the $\gamma$ phase, along the 50at.\%Al direction. However, Jewett et al. also claimed that there were two new ternary phases that existed and these were given the notation of T1 and T2. The location of the T1 and T2 phases are shown in the 1200°C isotherm of Figure 2.2. There was no structural information reported for the T1 and T2 phases, and only optical microscopy was used to support the existence of the T1 and T2 phases. It could not be ascertained whether the T1 and T2 phases were present at 1200°C, or whether they were decomposition products of higher temperature phase equilibria.

In recent years, there have been two studies published on the ternary phase equilibria from the same research group. One study was by Perepezko et al. [12] in 1990 and another study by Das et al. [22] in 1993. The primary purpose of these two studies was to determine the liquidus projection and to clarify the conflicting results from the earlier studies of the Nb-Ti-Al system.

The liquidus projection that was determined from the study by Perepezko et al. [12] is shown in Figure 2.3. This projection was consistent with the recent modifications to the binary Ti-Al phase diagram [15,16]. It showed that the $\alpha$ phase formed from the peritectic $L + \beta \rightarrow \alpha$ reaction at the higher temperature of $\approx 1480^\circ$C, compared to the $\gamma$ phase which formed from the peritectic $L + \alpha \rightarrow \gamma$ reaction at
Figure 2.3. Shows the liquidus projection of the ternary Nb-Ti-Al system determined by Perepezko et al. [12].
= 1450°C. There were two important points made from this liquidus projection. The first point was that the liquidus surface of the β phase covered an extensive portion of the ternary phase diagram. The second point was that the bivariant L + β + σ and L + σ + γ tie-triangles reacted in a class II four phase reaction [23] near the central portion of the liquidus projection. The product L + β + γ tie-triangle then moved toward the binary Ti-Al side, where it reacted in another class II four phase reaction with the L + β + α tie-triangle. The L + β + α tie-triangle had originally started from the binary peritectic L + β ↔ α reaction. The product of this reaction was the L + β + α tie-triangle, which terminated at the binary peritectic L + α ↔ γ reaction. Thus, these two points indicated that the solidification paths of alloys, that had compositions near the central portion of the ternary phase diagram, could have solidified with the β phase or could have complications near the four phase reactions.

Further work by Das et al. [22] indicated that refinements in the 1200°C isotherm had occurred near the composition of Ti₄Al₃Nb. The revised 1200°C isothermal section, which is currently accepted to be the most accurate representation of the high temperature phase equilibria in the Nb-Ti-Al system, is shown in Figure 2.4. The refinement made by Das et al. involved changing the phase for the region that had the Ti₄Al₃Nb composition from the T2 phase to the α phase. The T2 phase, which had been seen in the earlier 1200°C isothermal section of Figure 2.2, was identified as the ordered β (B2) phase. However, it was argued that the B2 phase had formed from the specific cooling methods employed, and was not considered to be an equilibrium phase. Likewise, the T1 phase was also found to have had the B2 phase, and was disregarded as an equilibrium phase by a similar argument used for the T2 phase.
Figure 2.4. Shows the 1200°C isothermal section of the ternary Nb-Ti-Al system determined by Das et al. [22].
Figure 2.5. Shows the partial sections of the isotherms in the ternary Nb-Ti-Al system determined by Das et al. [22]. (a) 1200°C; (b) 1150°C.
The α phase that was studied by Das et al. [22] was assumed to have the HCP structure since no structural results were reported in the study. Nevertheless, the phase boundaries near the Ti₄Al₃Nb composition of the α phase were shown to be complicated. The tie-lines surrounding this composition were significantly changed after just a 50°C drop in temperature from 1200°C. These are shown in the partial sections of the 1200°C and 1150°C isotherms in Figure 2.5. One of the most dramatic changes in the boundaries of the phase equilibria between 1200°C and 1150°C involved the presumed class II four phase reaction of the $\beta + \gamma + \alpha^*$ and $\beta + \gamma + \sigma$ tie-triangles (Figure 2.5a) to form the $\alpha^* + \sigma + \beta$ and $\alpha^* + \sigma + \gamma$ tie-triangles (Figure 2.5b). This reaction was shown to have shifted the tie-lines in the two-phase $\alpha^* + \sigma$ fields by nearly 90° from the two-phase $\beta + \gamma$ fields.

The combined results of Perepezko et al. [12] and Das et al. [22] also indicated that the B2 phase covered an extensive composition range in the central portion of the Nb-Ti-Al system. The extent of the B2 phase at 1200°C was shown previously in Figure 2.4. However, the compositional boundaries of the B2 phase were not precisely known.

2.1.2 The Ti-Based Alloy Development Studies

The phase equilibria and the microstructures that can be produced from various heat treatments of alloys in the Ti-rich part of the ternary Nb-Ti-Al system have been reviewed by Williams [1] and Rhodes [2]. These alloys show that a variety of microstructures can be produced by processing or heat treatments to form different morphologies, distributions and combinations of the equilibrium α and β phases, the metastable $\alpha'$ and $\alpha''$ martensites, and the metastable $\omega$ phase. The reason the different microstructures were produced was due to the existence of the β phase at
higher temperatures that could be stabilized down to room temperature with sufficient Nb additions.

The renewed interest during the 1980s in the development of Ti-aluminides prompted several studies of the phase equilibria in $\alpha_2$-Ti$_5$Al based alloys that contained up to 30at.%Nb additions. In 1988, a study by Banerjee et al. [13] showed that an orthorhombic phase (O-phase) formed in a Ti-25Al-12.5Nb (at.%) alloy that was heat treated at 1100°C and furnace cooled. This heat treatment produced equiaxed $\alpha_2$ grains in an ordered $\beta$ (B2-CsCl structure) matrix at 1100°C. The slow cooling rate resulted in the growth of the $\alpha_2$ grains, which caused the formation of the O-phase at the triple points of the impinged $\alpha_2$ grains. The O-phase was studied by selected area electron diffraction (SAED) and convergent beam electron diffraction (CBED) to show that the structure was consistent with the Cmcm space group and that the lattice parameters were $a = 4.50\,\text{Å}$, $b = 5.88\,\text{Å}$, and $c = 9.60\,\text{Å}$. The channelling enhanced microanalysis technique was used to determine the atomic site occupancy of the O-phase. This technique indicated that the composition of this phase was based on the Ti$_2$AlNb stoichiometry.

The presence of the O-phase was subsequently confirmed by Kaufman et al. [24] in 1988. However, the lattice parameters determined for the O-phase by Kaufman et al. were different than those determined by Banerjee et al. [13]. The O-phase was observed in Ti-25Al + Nb (at.%) alloys that contained at least 12at.%Nb and were heat treated between 800°C and 1000°C. The CBED analysis showed the O-phase to have the same Cmcm space group, but the lattice parameters were $a = 6.2\,\text{Å}$, $b = 9.4\,\text{Å}$, and $c = 4.7\,\text{Å}$. 
The temperature and composition range of the O-phase were investigated in several studies immediately following the discovery [25-35]. These studies contributed mainly to the understanding of the phase equilibria in the section of the phase diagram that connects the binary $\alpha_2$-Ti$_3$Al phase to the O-Ti$_2$NbAl phase. The Ti-27.5Al + Nb section shown in Figure 2.6 was developed from the results by Banerjee et al. [32], and is the currently accepted phase equilibria for this part of the ternary phase diagram.

Evidence showing the existence of a second ternary phase was reported in the study by Strychor et al. [36] in 1988. This evidence was obtained from low temperature heat treatments on alloys based on the composition of Ti$_3$Al alloys with ternary additions from 5 to 17at.%Nb. The alloys containing more than 5at.%Nb showed a rapid drop in the $M_s$ temperature of the $\alpha'$ martensite and retention of the $\beta$ phase, which had ordered to the B2 phase during cooling. Then, the metastable B2 phase was shown to have decomposed to an $\omega$-type phase during the low temperature heating. The SAED analysis of the $\omega$-type phase indicated that the structure was ordered and was consistent with the B8$_2$ structure, which was a HCP-Zr$_2$Al prototype structure.

The $\omega$-B8$_2$ phase was confirmed in a 1990 study by Bendersky et al. [37]. In this study, an alloy with the Ti$_4$Al$_3$Nb composition was heat treated at 700°C for 26 days. This caused the prior B2 matrix to transform completely to the $\omega$-B8$_2$ phase. Thus, the stoichiometric composition of the $\omega$-B8$_2$ phase was determined to be Ti$_4$Al$_3$Nb. The structure of the $\omega$-B8$_2$ phase was investigated using SAED and CBED analysis to show that the space group was P6$_3$/mmc, and the lattice parameters were
Figure 2.6. Shows the temperature-composition diagram of the Ti₃Al to Ti₅AlNb section by Banerjee et al. [32].
The mechanism of this transformation was also studied, but will be discussed later in section 2.3 on the omega phases.

There was a follow up study by Bendersky et al. [38] in 1990 that reported the possibility of another ordered derivative of the \( \omega \)-phase. In this study, an alloy with the composition of Ti-37.5Al-20Nb (at.\%) was heat treated at 700°C for 18 days. The results showed that small precipitates formed in the matrix of the \( \omega \)-B8\(_2\) grains. The SAED analysis indicated that the lattice parameters of the precipitates were \( a = 7.93\text{Å} \) and \( c = 5.52\text{Å} \). These lattice parameters of the precipitates were larger than those of the \( \omega \)-B8\(_2\) phase. Two possible structures of this ternary phase were proposed. One possible structure was based on the Pearson symbol hP18, which had the P6\(_3\)/mcm space group and Ga\(_4\)Ti\(_5\) prototype structure. The other possible structure was based on the Strukturberryicht D8\(_s\) structure, which had the P6\(_3\)/mcm space group and Mn\(_9\)Si\(_3\) prototype structure.

### 2.2 The Sigma Phase

The sigma (\( \sigma \)) phase occurs in many transition-metal alloy systems that are of technological interest in alloy development, such as the stainless steels and the superalloys. However, the occurrence of the \( \sigma \) phase in these alloys has usually been avoided because of its generally hard and brittle properties at room temperature. These properties have had a deleterious effect on the mechanical properties, since the \( \sigma \) phase usually forms along the grain boundaries of affected alloys, where cracks can nucleate and propagate. Conversely, the \( \sigma \) phase has a high melting point and a complex ordered structure, that may provide some strength and creep resistance at high temperatures. A full review of the structure and properties of the \( \sigma \) phase in various binary and ternary alloy systems is described by Hall and Algie [39].
The σ phase has been determined in the binary Nb-Al system to form by the peritectic \( L + \beta_1 \rightarrow \sigma \) reaction at \( \approx 1940^\circ C \) [40]. From Table 2.1, the stoichiometries of the \( \beta_1 \) and the σ phases were determined to be Nb₃Al and Nb₂Al, respectively. The maximum solubility of Al in binary compositions of the σ phase was 12at.%Al at \( \approx 1600^\circ C \). The range of ternary compositions of the σ phase in this system is shown in Figure 2.4 [12,20-22]. The ternary σ phase region was shown at 1200°C to extend from the binary Nb-Al side into the ternary Nb-Ti-Al system, along the constant Al composition section. The solubility range for Ti, in the ternary compositions of the σ phase, was estimated to be \( \approx 35 \)at.%Ti at 1200°C. The \( L + \beta_1 \rightarrow \sigma \) liquidus valley, which extends from the binary peritectic reaction into the ternary section, decreases with temperature, as shown in Figure 2.3.

The structure of the σ phase, based on the Nb₃Al stoichiometry, has been investigated by Wilson and Spooner [41,42]. This phase has been described as a topologically close packed (TCP) structure, since it can be viewed as consisting of distorted, hexagonal close packed, layers of atoms that are rotated by 90° between each alternating layer. Like the σ phases in other various alloy systems, the σ phase in the Nb-Al system has a tetragonal structure with the P4₂/mnm space group. The lattice parameters of the stoichiometric Nb₃Al composition were measured to be \( a = 9.935\AA \) and \( c = 5.169\AA \) [11]. However, the lattice parameters of the unit cell for this σ phase do change with the Al content. There are 30 atoms associated with the unit cell of the σ phase. These atoms are arranged with varying degrees of order, on five different lattice sites in the unit cell. The schematic shown in Figure 2.7 shows the five different lattice sites in the projection of the unit cell along the c axis of the σ phase. These five sites with their equivalent Wyckoff designations are A (2a), B (4f),
C (8i), D (8i2), and E (8j) [43]. The occupation of these sites by the Nb and Al atoms was found to consist of predominantly Nb atoms on the B, C, and E sites; mostly Al atoms on the A site; and a mixture of both Nb and Al atoms on the D site [42]. The coordination number does have an effect on this particular site occupancy. The B site has the largest coordination number (CN = 15), the A and D sites have the smallest (CN = 12), while the C and E sites have an intermediate value (CN = 14). Therefore, both the atomic size and electronic behavior can affect the specific site occupancy in the σ structure.

2.3 The Gamma Phase

The gamma (γ) phase from the binary Ti-Al system has received extensive research during the last ten years. This surge in research has been attributed to several attractive properties of the γ phase, such as low density, good oxidation resistance, and high temperature strength retention. The development of potential alloys based on this phase has resulted from studies on the phase relations; microstructural formation by processing; and microstructure-property relationships relating to oxidation, deformation, and fracture. Further information on these topics for the γ phase is provided in the review articles by Kim [7,44].

The formation of the γ phase in the binary Ti-Al system was recently modified to show that it solidified in the peritectic L + α → γ reaction at ≈ 1450°C, as shown in Figure 2.1. The solubility range of this phase extends more to the Al-rich side, rather than to the Ti-rich side, from the exact TiAl stoichiometry. In studies of the ternary Nb-Ti-Al system, the γ phase was found to have an extensive solubility range for Nb at temperatures in the 1200°C range [12,20-22]. These studies indicated that up to 26at.%Nb was soluble in the γ phase at 1200°C.
Figure 2.7. Shows the five lattice sites in the projection of the unit cell for the \( \sigma \) phase [41].
The structure of the $\gamma$ phase was determined to be the face-centered tetragonal L1$_0$ structure and the P4/mmm space group [10]. The unit cell of this structure has a layered arrangement of Ti and Al atoms on alternating (001) planes, as shown in Figure 2.8. The Ti atoms occupy the 1a and 1c Wyckoff sites at $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, 0)$, while the Al atoms occupy the 2e Wyckoff site at $(0, \frac{1}{2}, \frac{1}{2})$ and $(\frac{1}{2}, 0, \frac{1}{2})$. The lattice parameters, for this equiatomic TiAl composition, were determined to be $a = 3.976\text{Å}$ and $c = 4.049\text{Å}$ [45]. However, these lattice parameters also depended on the Al content. Measuring these changes in the lattice parameters by the $c/a$ ratio showed that the $c/a$ ratio increased from $\approx 1.02$ to $\approx 1.03$ with increasing Al content [46].

The atomic site occupancy of the $\gamma$ phase, containing ternary additions of Nb, was studied by Kronitzer et al. [47] and Jackson [48]. Kronitzer et al. showed that Nb atoms randomly occupied the 1a and 1c Wyckoff sites with the Ti atoms, for small additions of Nb to the $\gamma$-TiAl phase. In comparison, Jackson reported the existence of a new phase that was based on the tetragonal L6$_0$ structure and P4/mmm space group. This structure showed the Ti atoms occupied the 1a Wyckoff site, the Nb atoms occupied the 1c Wyckoff site, and the Al atoms occupied the 2e Wyckoff site. Thus, the new structure reported by Jackson showed that ordering had occurred between the Nb and Ti atoms on the 1a and 1c Wyckoff sites. The occurrence of this ordering reaction from the $\gamma$-L1$_0$ structure was supported by the observation of APDBs in the $\gamma$-L6$_0$ structure.

### 2.4 The B2 Phase

The B2 phase has been shown to exist in alloys of the Nb-Ti-Al system at both high temperatures and over large composition ranges. The composition range of alloys that had been found to contain the B2 phase included compositions in the
Figure 2.8. Shows the unit cell of the $\gamma$-TiAl phase.
central portion of the ternary phase diagram [12], compositions close to Ti₃Al containing Nb additions in the range of ≈5Nb to 30Nb (at.%) [13,24-35], the Ti₄Al₃Nb composition [37], and binary Nb-Al compositions with additions of 13.5Al to 16.9Al (at.%) [49]. The 1200°C isotherm by Das et al. [22] showed that the solid solution range of the B2 phase was fairly small and was located close to the center of this ternary system, as shown in Figure 2.5. The temperature of the β to B2 transition was determined to increase with an increase in the Nb content of alloys based on the approximate Ti₃Al composition. More specifically, the β to B2 transition temperature was found to increase from ≈1100°C for 12.5at.%Nb additions to over 1400°C for 25at.%Nb [13,24-26,28-31,33-35]. Likewise, a high transition temperature of more than 1400°C was suggested by Bendersky et al. [37] for an alloy with a Ti₄Al₃Nb composition. The B2 phase was also recently observed in binary Nb-13.5Al and Nb-16.9Al (at.%) alloys after being heat treated at only 800°C for 10 hours [49]. This B2 phase was determined to be a metastable phase that had formed, instead of the equilibrium Nb₃Al (β₁) phase, at the low aging temperature. The formation of the B2 phase, instead of the β₁ phase, was possible because the activation energy of the second order β to B2 transition was lower than that of the first order β to β₁ transition. Therefore, the diffusion length that was required to form the B2 phase was shorter and the formation of the B2 phase occurred, rather than the β₁ phase.

The B2 phase has the ordered BCC (CsCl) structure and the Pm₃m space group. The atomic site occupancy of the B2 phase in a Ti-25Al-10Nb (at.%) alloy was determined by Banerjee et al. [50] using channelling enhanced microanalysis. The composition of the B2 phase in the two phase α₂ + B2 microstructure of this alloy was found to be Ti-24.5Al-14Nb (at.%). The channelling results of the B2 phase indicated
that the two distinct sublattices in the B2 unit cell were occupied mostly by Ti on the 1a Wyckoff site at (0, 0, 0) and by a mixture of Ti, Nb, and Al on the 1b Wyckoff site at (½, ½, ½). The exact atomic percent values that were determined for the two sites were 48Ti and 2Nb for the 1a site, and 14Ti, 12Nb, and 24Al for the 1b site. The schematic shown in Figure 2.9 shows the B2 unit cell using the atomic site occupancy determined by Banerjee et al.

A 1988 study by Strychor et al. [36] showed that the B2 phase in Ti₃Al + Nb alloys exhibited diffuse scattering and extra maxima in the selected area electron diffraction (SAED) patterns, and tweed microstructures in the TEM images. The diffuse scattering and extra maxima in the SAED patterns was interpreted to show an instability in the B2 lattice that suggested two possible modes of transformation. The first mode was determined from the observation of diffuse scattering at the 1/3<111> positions in the SAED patterns of the B2 matrix. This diffuse scattering was attributed to 2/3<111> longitudinal displacement waves, or phonons, that led to the formation of an ordered α-type phase during low temperature aging of Ti₃Al + Nb alloys. The second mode was determined from the observation of diffuse streaks that ran parallel to the <110> directions and extra maxima at 1/2{110} positions in the SAED patterns of the B2 matrix. These observations were attributed to 1/2<110>{110} type transverse lattice displacement waves, that caused localized strain in the B2 lattice, which led to the formation of the tweed microstructure. These shear strains were shown to be consistent with the lattice deformation of the martensitic transformation of the 2H pseudo ortho/hex (orthorhombic/hexagonal) structure from the B2 phase. The diffuse streaking and extra maxima observed in
Figure 2.9. Shows the unit cell of the B2 phase with the atomic site occupancy determined in a Ti-24.5Al-14Nb (at.%) alloy by Banerjee et al. [50].
the SAED patterns were formed from the tweed microstructure, and were explained as rel-rods that intersected the Ewald sphere.

This tweed microstructure has been observed in the B2 phase of many alloy systems that exhibited martensitic transformations [51]. This relationship between the tweed microstructure and the martensitic transformation in these types of alloys has been investigated by Robertson and Wayman [52-54], Tanner et al. [55], and Schryvers and Tanner [56]. Robertson and Wayman showed that the tweed microstructure was formed by \( <110>{\{1\bar{1}0} \) static displacement waves, which resulted in the softening of the elastic constant \( C' \), where \( C' = \frac{1}{6}(C_{11} - C_{12}) \), in the B2 phase of a 63Ni-37Al (at.\%) alloy. Tanner et al. and Schryvers and Tanner showed that the tweed microstructure in the B2 phase of the 63Ni-37Al (at.\%) alloy was composed of a fine-scaled mosaic assembly of non-uniformly distorted and micromodulated domains, which were coined inhomogeneously strained domains (ISDs). The ISDs were examined by high resolution electron microscopy (HREM). The ISDs were shown to lie parallel to \{110\} plane traces in the B2 matrix and to have a size of \( \approx 40-60\AA \) in length, with an average spacing of \( \approx 13\AA \) thick. The computer simulations by Schryvers and Tanner confirmed that the atomic structure of the ISDs was consistent with small transverse shuffles, plus shear distortions of the \( <110>{\{1\bar{1}0} \) type. The displacements in the ISDs were correlated with the low energy transverse \( \Sigma 4 (\zeta\zeta0) \)-TA\(_2\) phonon mode that was found to have an anomalous, temperature-dependent, incomplete softening at \( \zeta \approx 0.16 \). It was theorized that the ISDs were formed by the dynamic softening of the \( C' \) constant, which resulted from the TA\(_2\) phonon that became coupled to the static strain fields of defects in the B2 lattice. It
was suggested that the nucleation site of the martensitic phase was determined by the strength of the strain field that was associated with the defect.

2.5 The Omega Phase

The omega (ω) phase has been an intriguing phase that was first discovered in thermally aged, β-stabilized, titanium alloys in 1954 [57]. Since then, it has been observed in the group IV transition elements of Ti, Zr, and Hf; in numerous alloys that consisted of the group IV elements; and in the elements immediately to the right of the group IV elements (the d-rich transition elements of Nb, V, and Mo) [58]. The ω phase has also been observed in many alloys that were not based on the group IV elements, such as: Cu-Zn [59,60], Cu-Sn [59,61], Cu-Zn-Al [62], Cu-Zn-Si [63], Cu-Al-Ni [64], Ag-Al [65], Ag-Mg [66], Fe-Al [67], and Ni-Al [68]. One of the main reasons for investigating the ω phase was because of the harmful effect this phase has on the mechanical properties of these alloys. The formation of the ω phase has been shown to embrittle the alloy by decreasing the ductility and increasing the hardness. Extensive studies have been conducted on the morphology; the effects on the physical properties; the nature of the diffuse x-ray, electron, and neutron scattering; the transformation kinetics; and the transformation mechanism of the ω phase. The results of these studies were summarized in a review article by Sikka et al. [58].

The ω phase that forms in Ti has been suggested to be the low-temperature high-pressure modification of the β phase [69]. Normally, the α-HCP phase is the stable phase in the unary Ti system below the allotropic transition of ~882°C at atmospheric pressure. However, the ω phase has been shown at high pressures to be the stable phase, instead of the α phase, based on the equilibrium unary P-T diagram that was developed for Ti [58]. The structure of the ideal ω phase in pure Ti was
found to be the HCP structure, with the P6/mmm space group. The unit cell of this ideal phase contains three atoms: one atom located on the 1a Wyckoff site at (0, 0, 0) and two atoms located on the 2d Wyckoff site at (\(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\)) and (\(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\)). However, the \(\omega\) phase has also been shown to have the trigonal structure with the P\(\overline{3}\)m\(\overline{1}\) space group in Ti-based alloys. The difference in the symmetry between the \(\omega\)-trigonal and \(\omega\)-HCP phases was due to the small atomic displacement of the two atoms on the 2d Wyckoff site in the \(\omega\)-HCP phase. Thus, the atomic site occupancy of the \(\omega\)-trigonal phase was shown to have one atom located on the 1a Wyckoff site at (0, 0, 0) and two atoms located on the 2d site at (\(\frac{1}{2}, \frac{1}{2}, z\)) and (\(\frac{1}{2}, \frac{1}{2}, \bar{z}\)). The \(z\) parameter indicates the magnitude of the atomic displacement and that the displacement occurs in the direction of the c-axis in the trigonal unit cell.

The \(\beta\) to \(\omega\) transformation has been described by a plane collapse mechanism that involves three \{111\}_b planes. In this mechanism, one pair of planes collapses together to an intermediate position, while the third plane remains unaltered [58]. The atomic displacements that were required for this transformation have been described by a soft-mode transformation mechanism. This mechanism involves a longitudinal sinusoidal wave with atomic displacements, \(U = W\sin[q_\omega x + \phi(x)]\); a wave vector, \(q_\omega = 2/3<111>2\pi/a_p\); a phase for the three possible variants, \(\phi(x) = 0, 2\pi/3, 4\pi/3\); and an amplitude, \(W = a_p/6\) for \(\omega\)-HCP or a value less than this for \(\omega\)-trigonal. The \{111\}_b plane collapse mechanism and the soft mode mechanism of the \(\beta\) to \(\omega\) transformation are shown in the schematic of Figure 2.10. This schematic shows the projection of both the (110)_b planes for the \(\beta\) phase and the (1120)_\(\omega\) planes for the \(\omega\) phase. If the collapse of the two \{111\}_b planes is incomplete, then the atoms on the B
plane are displaced. This results in a rumpled B plane and the trigonal symmetry for the ω phase.

The transformation of the β phase to the ω phase has been shown to form twelve variants of the ω phase. These variants were formed from the orientation relationship that the ω phase has with the β phase:

\[(0001)_ω \parallel \{111\}_β \quad \text{and} \quad <1120>_ω \parallel <1T0>_β.\]

The twelve variants were formed from four rotational variants that each had three translational variants, as shown in the schematic of Figure 2.11. The two rotational variants were formed by aligning the \((0001)_ω\) plane parallel to either the \((1\overline{1}1)_β\) or \((1\overline{1}1)_β\) planes of the β phase. The three translational variants were determined from the \(\{111\}_β\) plane that remained unaltered during the plane collapse. Since the stacking sequence of the \(\{111\}_β\) planes in the BCC β phase is \(…ABCABC…\), then the \((0001)_ω\) plane of the A-variant is formed from the A plane, the B-variant from the B plane, and the C-variant from the C plane. Therefore, six out of the twelve total variants are illustrated in the schematic of Figure 2.11.

There have been several studies in the past that have investigated the influence of Nb on the formation of the ω-type phase in binary Ti-Nb alloys [70-73]. These studies have shown that the ω phase can transform both athermally and isothermally from the β phase in the Nb-Ti alloys. The primary difference between the two formation mechanisms was that the composition of the athermal ω phase was the same as that of the β matrix, while the composition of the isothermal ω phase was different from that of the β matrix. However, the isothermal ω phase was determined to form from the β matrix by the same mechanism as the athermal ω phase, which involved the collapse of alternating pairs of \(\{111\}_β\) planes.
Figure 2.10. Shows the \{111\}_\beta plane collapse model of the \beta to \omega transformation. The view is normal to the (110)_\beta planes.
Figure 2.11. Shows two rotational variants, each one containing three translational variants, of the $\omega$ phase formed from the $\beta$ to $\omega$ transformation. The view is normal to the (110)$_\beta$ planes.
The most systematic studies of the \( \omega \) phase in the binary Nb-Ti system were by Moffat and Larbalestier [72,73]. In these studies, the effect of cooling rate and isothermal aging were investigated in alloys that contained 20Nb to 35Nb (at.%). The results of these studies showed that there was a competition between the formation of the \( \omega \) phase, the metastable \( \alpha'' \) martensite, and the equilibrium \( \alpha \) phase depending on the cooling rate from 1000°C and the isothermal aging temperature. It was shown that water quenching caused the formation of the \( \alpha'' \) martensite, while air cooling and furnace cooling caused the formation of the \( \omega \) precipitates. The aging experiments indicated that the equilibrium \( \alpha \) phase was formed at the higher aging temperatures, such as 400°C to 500°C, while the lower aging temperatures, such as 200°C and 300°C, caused the formation of the \( \omega \) phase. The competition between the \( \alpha'' \) martensite and the \( \omega \) precipitates in the alloys was determined to have resulted from the lowering of the \( M_s \) (martensite start) temperature of the \( \alpha'' \) martensite by the addition of >20at.%Nb [72]. It was also suggested by Moffat and Larbalestier that since the \( \omega \) and \( \alpha'' \) phases were never observed together in the microstructure, then which ever phase formed first excluded the other phase from forming.

There have been a only a few studies that have investigated the formation of the \( \omega \)-related phases in ternary Nb-Ti-Al based alloys [36-38]. The study by Strychor et al. [36] was the first to show that ordered derivatives of the \( \omega \) phase were formed in Ti\(_3\)Al + 5Nb to 17Nb (at.%) alloys. The \( \omega \)-related phase that formed in these water quenched samples was detected only in the SAED patterns of the B2 matrix. These diffraction patterns showed diffuse streaking and extra diffraction maxima at \( 1/3\{111\}_\beta \) positions that were attributed to an ordered derivative of the \( \omega \)-related phase. The effect of isothermal aging for different times at 400°C and 500°C was
found to slowly degrade the tweed pattern of the B2 matrix and to intensify the reflections of the ordered ω-related phase in appropriate SAED patterns. Strychor et al. determined that the ordered ω-related phase had the B8₂ structure, which consisted of the P6₃/mmc space group. The ω-B8₂ structure was found to have A₂B ordering, where it was assumed that the A represented a mixture of Ti and Nb atoms and the B represented the Al atom.

The transformation mechanism of the ω-B8₂ phase from the B2 phase in a Ti₄Al₃Nb alloy was investigated by Bendersky et al. [37]. This study showed that furnace cooling from 1400°C resulted in the transformation of the B2 matrix completely to the trigonal ω"-type phase. This ω"-type phase was determined by CBED to have the P3m1 space group. It was deduced from microstructural evidence that the B2 phase was stable at 1400°C, and that the subsequent heat treatment of a furnace cooled sample for 26 days at 700°C resulted in the transformation of the ω-B8₂ phase from the ω" matrix. The site occupancies of the ω" and ω-B8₂ phases were determined by X-ray diffraction. This analysis showed that the Nb atoms flowed out of sites on the collapsed double layers and into sites on the single layers. The vacated sites on the double layers were then preferentially occupied by Ti and Al atoms, and the sites on the single layers were enriched by a mixture of Nb, Ti, and Al atoms. The driving force for the chemical exchange between these atoms was shown to be from the maximization of the Ti-Al bonds on the double layers. This conclusion was based on the fact that the sites on the double layers had a greater coordination number of nearest neighbors than those on the single layers in the ω" and ω-B8₂ phases. The Ti and Al atoms were shown to have a preference for the sites on the
double layers, since the Ti-Al bonds were the most stable and had the shortest bond length compared to the other possible types of bonds.

In the study by Bendersky et al. [37] the transformation of the parent B2 phase to the final \( \omega \)-B8\(_2\) phase was described by a series of structural changes that involved subgroup/symmetry relations in crystallography [43]. The transitions that described the B2 to \( \omega \)-B8\(_2\) phase transformation are shown in the schematic of Figure 2.12. These individual transitions were connected together by subgroup/supergroup relations that indicated how many variants of the product phase were formed from the parent phase, whether the symmetry in the product phase was increased or decreased relative to the parent phase, and whether there was chemical ordering or whether distortions had occurred. The symmetry and atomic site occupancy results were then used to show that the transformation path from the B2 phase to the \( \omega \)-B8\(_2\) phase traversed the trigonal \( \omega^\prime \) phase. This trigonal \( \omega^\prime \) phase had the lowest symmetry as compared to either the B2 or \( \omega \)-B8\(_2\) phases. The transitions from the B2 phase to the \( \omega^\prime \) phase occurred during furnace cooling, since these transitions involved only the partial collapse of the double layers and the incomplete exchange of atoms between double and single layers. However, the transition from the \( \omega^\prime \) phase to the \( \omega \)-B8\(_2\) phase required thermal energy, since it involved the full collapse of the double layers, the complete chemical exchanges that led to the disordered single layers, and the fully populated sites on the double layers by Ti and Al atoms.

2.6 The Ortho/Hex Phases

The ortho/hex phases are the phases with the closely related HCP and orthorhombic structures that have been observed in the Ti-rich alloys of the Nb-Ti-Al system. These phases are formed from alloys with compositions that show the \( \beta \) or
Figure 2.12. Shows the transformation paths from the β phase to the ω-related phases using subgroup and symmetry relations from Bendersky et al. [37].
B2 phase to be stable at high temperatures. This stable β or B2 phase can then be quenched and retained at room temperature, or it can undergo a variety of transformations to different HCP and orthorhombic phases depending on the composition, heat treatment, and cooling rate. Thus, the studies of these different HCP and orthorhombic phases are divided into two different groups: the disordered structures of the α, α', and α'' phases in binary Nb-Ti alloys and the ordered structures of the α₂, α₂', and O (orthorhombic) phases in ternary Ti₅Al + Nb alloys, with constant Al content. This division facilitates a comparison of the influences of Nb and Al on the structure and transformation of these phases in the Ti-rich alloys.

2.6.1 Disordered Structures

The HCP and orthorhombic phases that were observed in the binary Nb-Ti alloys consisted of the equilibrium α phase and the metastable α' and α'' martensite phases. Both equilibrium and metastable have disordered site occupancies between the Nb and Ti atoms. The structure of the equilibrium α phase was determined to be the HCP structure and the P6₃/mmc space group [10]. The metastable α' phase was determined to have formed instead of the α phase when a martensitic transformation occurred by rapid cooling from the high temperature β phase in Ti-based alloys containing up to ≈7at.%Nb [72,74]. The structure and the lattice parameters of the α' phase were identical to the α phase. For binary alloy compositions greater than ≈7at.%Nb, the α'' phase was determined to have formed instead of the α' phase by a similar martensitic transformation from the β phase [72]. The α'' phase was found to have the C-centered orthorhombic structure and Cmcm space group [75].

The orthorhombic structure of the α'' phase resulted from distortions between the Nb-Ti bonds. These distortions became more noticeable in binary alloys that
contained more than =7at.%Nb [72]. The range in compositions for the distortions in the a and b lattice parameters, as measured by the a/b ratio, increased with the Nb content from 0.578 for =7at.%Nb to 0.654 for 20at.%Nb [74]. It was also determined that the orthorhombic structure of the α" phase was produced from the α'-HCP structure by varying the positions of the atoms on the Wyckoff sites in the α" phase [72]. There were four lattice sites in the Cmcm space group of the α" structure that could be described by the 4c Wyckoff site [43]. The atomic positions of these 4c sites were (0, y, ¼); (0, y, ¾); (½, y+½, ¼); and (½, y+½, ¾). The distortion in the orthorhombic structure was indicated by the y parameter, which was =0.2 for Ti-Nb alloys [76]. The y parameter for the HCP structure in Ti-Nb alloys was 0.1667. This value for the y parameter of the HCP structure was based only on the a/b ratio, and would produce the ideal a/b ratio of 0.578 for the undistorted HCP structure.

The Ms temperature of the martensitic transformation for the α' and α" phases was determined by Jepson et al. [74] and Moffat and Larbalestier [72] to be dependent on the Nb content of the binary Nb-Ti alloys. The study by Jepson et al. showed that the Ms temperature dropped rapidly from ≈850°C in Ti to ≈300°C in the Ti-17.at.%Nb alloy. The study by Moffat and Larbalestier showed that the Ms temperature fell below room temperature in alloys that contained more than ≈30at.%Nb. This conclusion was based on the observation that the retained β phase was the only phase that was observed in alloys of these compositions after water quenching from 1000°C.

Jepson et al. also showed that the Ms temperature was a function of cooling rate in the binary Nb-Ti alloys. It was found that rapid cooling rates could suppress
the martensitic transformation of the $\alpha''$ phase. From this result, it was suggested that the $\alpha''$ structure could form both isothermally and martensitically.

2.6.2 Ordered Structures

The equilibrium $\alpha_2$ and O phases and metastable $\alpha_2'$ phase form in ternary Ti$_3$Al + Nb alloys with ordered structures. It was determined that the $\alpha_2$ and $\alpha_2'$ phases formed in Ti$_3$Al + Nb alloys with less than $\approx$ 11at.%Nb [24,26,27]. The $\alpha_2$ phase has the HCP structure with the Ti$_3$Al stoichiometry and P6$_3$/mmc space group [10]. The ordering between Ti and Al in the $\alpha_2$ structure causes the a-axis lattice parameter to be twice the a-axis lattice parameter of the disordered $\alpha$-Ti structure. The $\alpha_2'$ phase has the same HCP structure and lattice parameters as the $\alpha_2$ phase, but has been shown to form by a martensitic transformation during rapid cooling from the high temperature $\beta$ phase [24,26,27]. The O phase forms in Ti$_3$Al + Nb alloys that contain more than $\approx$12at.%Nb [13,24-32]. The O phase has the C-centered orthorhombic structure with the Ti$_2$AlNb stoichiometry and Cmcm space group [13].

In Ti$_3$Al + 0-11at.%Nb alloys, the $\alpha_2$ and $\alpha_2'$ phases can both form from the high temperature $\beta$ or B2 phase during cooling. However, only the equilibrium $\alpha_2$ phase can form during isothermal heating of alloys containing the retained $\beta$ phase. In fact, the $\alpha_2$ and $\alpha_2'$ phases are so cooling rate dependent, that it is possible to retain the high temperature disordered $\beta$ phase that exists over these composition ranges by rapid quenching. This disordered $\beta$ phase then orders to the B2 phase at lower temperatures in alloys that contained more than $\approx$5at.%Nb [24]. The metastable $\alpha_2'$ phase usually forms by martensitic transformation for most cooling rates. In comparison, the equilibrium $\alpha_2$ phase forms by nucleation and growth processes only at high temperatures and for extended periods of time [27,32,35]. This
equilibrium $\alpha_2$ phase can form from the $\beta$ phase as grain boundary allotriomorphs, intragranular plates, and equiaxed grains depending on the alloy composition and thermomechanical history.

The $M_s$ temperature of the martensitic transformation has been shown to decrease rapidly in the $\text{Ti}_3\text{Al} + \text{Nb}$ alloys with increasing Nb content [24,26,27,36]. In the binary $\text{Ti}_3\text{Al}$ alloy, the martensitic transformation was found to be impossible to suppress by rapid cooling [77]. The $\alpha'_2$ phase that formed in this martensitic transformation occurred by first forming the $\alpha'$ phase and then ordering to the $\alpha'_2$ phase. In ternary $\text{Ti}_3\text{Al} + \text{Nb}$ alloys, the $\alpha'_2$ martensitic transformation could be suppressed completely, provided that the cooling rate was rapid enough. A very high cooling rate, such as by splat quenching, was necessary to suppress the martensitic transformation in a $\text{Ti}_3\text{Al} + 5\text{at.}\%\text{Nb}$ alloy, but a lower cooling rate could achieve the same result in alloys with higher Nb content [24]. For the alloy compositions and cooling rates that showed the occurrence of the $\alpha'_2$ martensitic reaction, it was suggested that plates formed with the $\alpha'$ phase first and then later ordered to the $\alpha'_2$ phase [27]. The development of this transformation sequence was based on the observation of midribs and anti-phase domain boundaries (APDBs) in the plates. These APDBs were the same as those that were observed in the $\alpha$ to $\alpha_2$ ordering reaction of binary $\text{Ti}_3\text{Al}$ based alloys [78].

The formation of the O phase in $\approx\text{Ti}_3\text{Al} + \text{Nb}$ alloys with Nb contents of $\approx 12$ to $30\text{at.}\%\text{Nb}$ requires thermal activation, since water quenching these alloys from high temperatures retains the $\beta$ phase with the B2 structure at room temperature [13,24-35]. Therefore, the O phase observed in these studies has been found to form only by slowly cooling from the high temperature $\beta$ or B2 phase, or by isothermally heating
the retained β phase. The main points concerning the O phase that were determined from these studies were the O phase was structurally related to the α₂ phase [13], the O phase could form from the B2 phase by a shearing mechanism that involved thermally activated processes [27,29], the O phase could form from the B2 phase by a composition invariant transformation [31], the transformation of the O phase could be described crystallographically [33,34], and the O phase could exist with two different atomic site occupations [31,35]. The details of these points are covered in the following discussion.

The O-Ti₂AlNb phase was found to be structurally related to the α₂-Ti₃Al phase and to involve additional ternary ordering that caused small orthorhombic distortions [13]. The structural relationship between these two phases is shown in the schematic of Figure 2.13. The atomic site occupancy of the α₂-Ti₃Al phase shown in Figure 2.13a consists of Ti atoms on the 6h Wyckoff sites and Al atoms on the 2d Wyckoff sites [43]. Kronitzer et al. [47] showed that the addition of Nb to the α₂ phase, in amounts that remained in solid solution, preferentially occupied the 6h sites with Ti atoms. However, in Ti₃Al + Nb alloys that contained more than ≈12at.%Nb, the O-Ti₂AlNb phase was found to form instead of the α₂ phase [13,24-33]. The O-Ti₂AlNb structure shown in Figure 2.13b involved further ternary ordering of the α₂ phase that caused the unit cell to be distorted in the direction of the a-axis and b-axis lattice parameters which are contained in the (001) planes. In the O-Ti₂AlNb structure, the Ti, Nb, and Al atoms were determined to predominantly occupy three different lattice sites. These were the 8g Wyckoff site by Ti, the 4c1 Wyckoff site by Nb, and the 4c2 Wyckoff site by Al [13,28]. Mozer et al. [28] performed a structural refinement using a sample that had the composition of Ti-25at.%Al-25at.%Nb to
Figure 2.13. Shows the relationship between the crystal structures of the $\alpha_2$-Ti$_3$Al phase and the O-Ti$_2$AlNb phase. (a) the $\alpha_2$-Ti$_3$Al phase (P6$_3$/mmc space group); (b) the O-Ti$_2$AlNb phase (Cmcm space group). The dark shaded atoms are at $z = 0$ and the light atoms are at $z = \frac{1}{4}c$. 
determine the relative atomic occupancies of the three different Wyckoff sites in the O-Ti$_2$AlNb structure. The results of this study showed that the Nb atoms occupied \( \approx 18\% \) of the 8g sites which were Ti-rich, and that the Ti atoms occupied \( \approx 18\% \) of the 4c1 sites which were Nb-rich. The 4c2 site was found to be occupied by only Al atoms.

The effect of the Nb content on the distortions in the O-Ti$_2$AlNb phase was studied by Kestner-Weykamp et al. [26]. These distortions were measured by the a/b ratio and were found to increase from \( \approx 0.632 \) for the O-Ti$_2$AlNb phase containing 20at.%Nb to \( \approx 0.645 \) for the O-Ti$_2$AlNb phase containing 30at.%Nb.

The O-phase has been found to form from the \( \beta \) phase as plates by a lattice shear mechanism in the studies by Kestner-Weykamp [27] and Bendersky et al. [29]. Kestner-Weykamp examined plates that formed during air cooling from the \( \beta \) phase, which was present at 1250°C, in a Ti$_3$Al + 20at.%Nb alloy [27]. These plates contained defect structures that consisted of midribs, columnar APDBs, and \{110\} twins aligned roughly parallel to the midrib. From the analysis of these defects, the \( \beta \) to O transformation was determined to be by a lattice invariant shear mechanism, that initially formed the orthorhombic \( \alpha'' \) shear product with the plate shape and then later ordered to the O structure. A subsequent diffusional growth mechanism was used to explain the thickening of the plates and the formation of the columnar shaped APDBs.

The formation of the O phase from the retained B2 phase during isothermal heating of two alloys was investigated by Bendersky et al. [29]. The two alloys examined in this study had compositions of Ti-12.2Al-37.2Nb and Ti-23.9Al-25Nb (at.%). Following the heat treatment at 700°C for 26 days, the O phase was observed as plates in the Ti-12.2Al-37.2Nb alloy and as equiaxed grains in the Ti-23.9Al-25Nb
alloy. The plates were determined by energy dispersive X-ray spectroscopy (EDX) analysis to have the Ti$_2$AlNb composition. This composition of the plates was different than the composition of the B2 matrix, which was Ti-10Al-45Nb (at.%) composition. However, the transformation of the plates was still described using the minimization of elastic strain energy approach which was consistent with the phenomenological theory of martensitic transformations [79]. This theory accurately predicted the habit plane and rigid body rotation of the plates using the measured lattice parameters of the B2 and O phases in this alloy. It was determined for the Ti-23.9Al-25Nb alloy that the formation of the equiaxed grains involved two steps: initially the retained B2 phase transformed completely to a highly faulted O phase and then later recrystallized into fault free grains.

The formation of the O phase from the B2 phase in a Ti-24Al-15Nb (at.%) alloy was described by a composition invariant transformation mechanism in the study by Muraleedharan et al. [31]. This alloy was heat treated for short times that lasted from one to sixty minutes at temperatures of 800°C, 900°C, and 950°C. The shorter aging times and lower temperatures favored the complete transformation of the retained B2 phase to the O phase without a change in composition. The O phase formed as plates, which contained complex defect structures determined to be coarse APDBs with the displacement vector of $1/4[110]$, fine APDBs with the displacement vector of $1/2[100]$, and stacking faults with the displacement vector of $1/10[025]$. The coarse APDBs observed in the O plates were shown to have the same size and a related displacement vector to the APDBs that were observed in the retained B2 matrix prior to aging. The presence of these APDBs with no variance in composition supported the conclusion in this study that the transformation from the B2 phase to
the O phase occurred by a shear type mechanism. However, this transformation
mechanism did require short-range diffusion, since the fine APDBs observed in the
O plates were formed from an ordering reaction that required atomic exchanges
between lattice sites.

Bendersky et al. [33,34] described the formation of the O phase from the high
temperature β phase using a crystallographic model based on a sequence of structural
changes related by subgroup and symmetry relations. Three alloys with compositions
of Ti-25Al-12.5Nb, Ti-25Al-25Nb, and Ti-28Al-22Nb (at.%) were examined after
heating at 1100°C for four days. This heat treatment caused the partitionless
transformation of plates in these three alloys. The analysis showed different defect
structures in the plates of the Ti-25Al-12.5Nb composition as compared to those in
the two Nb-rich alloys. From the identification of these defect structures, such as
APDBs and stacking faults, the transformation of the plates in the Ti-25Al-12.5Nb
alloy was shown to have occurred from the disordered β phase, while the
transformation of the plates that formed in the two Nb-rich alloys occurred from the
B2 phase. These results were then used to show that the plates present in these
alloys formed along two different transformation paths, as shown in Figure 2.14. The
plates in the Ti-25Al-12.5Nb alloy formed from the disordered β (Im3m) phase and
then followed the path that passed through the intermediate HCP structures before
reaching the final O structure. In comparison, the plates observed in the two Nb-rich
alloys formed from the B2 phase and then followed the path through the B19
structure to the final O structure. There was no structural confirmation of the
intermediate transitional structures in each of these two paths. However, evidence of
Figure 2.14. Shows the transformation paths from the $\beta$ phase to the $O$ phase using subgroup and symmetry relations from Bendersky et al. [33].
the individual transitions was obtained from the analysis of the defect structures in the plates and from the partitionless nature of the transformation in these alloys.

The O phase has been found to exist in two structural forms with different atomic site occupancies according to studies by Muraleedharan et al. [31,35]. In the first study by Muraleedharan et al. in 1992, the O phase was formed at the lower temperature of 800°C in the Ti-24Al-15Nb alloy and was determined to have the commonly observed site occupancy of Ti on the 8g Wyckoff site, Al on the 4c1 Wyckoff site, and Nb on the 4c2 Wyckoff site. However, the O phase that formed at the slightly higher temperature of 900°C showed a different site occupancy. This O phase was determined to have a random occupancy of Nb and Ti on the 8g and 4c2 Wyckoff sites, while Al still occupied the 4c1 Wyckoff site. In a recent study by Muraleedharan et al. in 1995, the same results showing two different site occupancies for the O phase were obtained from a series of heat treatments that were conducted on Ti-27.5at.%Al alloys with up to 25at.%Nb additions. In both studies, the site occupancies of the two different O phases were determined from intensity variations between reflections in the CBED patterns and by channelling enhanced microanalysis. The CBED analysis was conducted in thin regions of the O phase to minimize the dynamical scattering effects. The order parameter (S) was defined in terms of the Ti and Nb site occupation of the 8g and 4c2 Wyckoff sites. This parameter was calculated by thermodynamic analysis and showed that a random site occupancy between Ti and Nb atoms on these two lattice sites was stabilized at higher temperatures. Thus, it was suggested in both of these studies that Al stabilized the disordered α" martensite structure. This disordered α" martensite structure is a metastable phase that forms in the binary Nb-Ti system and then
orders into the ordered O phase, which is an equilibrium phase that forms in the ternary Nb-Ti-Al system.
3.1 Material

The compositions of the alloys used in this investigation were specified to Pratt and Whitney, who then manufactured the alloys. Out of a total of ten alloy compositions originally manufactured, the results of three alloys were used in this study. The nominal compositions of these three alloys (referred to as alloys 2, 3, and 4) are given in Table 3.1.

The main criterion for selecting the three alloy compositions was that each contain the BCC β phase in the microstructures at high temperatures. Therefore, the alloy compositions were chosen based on the 1200°C isotherm shown in Figure 2.2, which was developed from previous studies of the ternary Nb-Ti-Al phase diagram [17-20]. Thus, it was expected that at 1200°C the microstructures of alloy 3 should consist of a single β phase and alloys 2 and 4 should consist of the β + x phases, where x is the γ phase (alloy 2) or the σ phase (alloy 4). One of the purposes of this investigation was to then construct the phase equilibria for the alloys at higher temperatures than 1200°C.

The alloys were supplied by Pratt and Whitney in the form of 200 gram arc-melted samples. The as-received samples had been arc melted a total of four to six times to ensure complete chemical mixing. This was verified by composition line profiles performed on cross sections of the as-received samples using the Electron Microprobe Analyzer (EMPA). These profiles did not show significant chemical
Table 3.1. The nominal compositions of the as-received alloys and the compositions determined by microprobe analysis of the re-arc melted alloys.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Analysis Method</th>
<th>Nb (at.%)</th>
<th>Ti (at.%)</th>
<th>Al (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Nominal</td>
<td>27</td>
<td>33</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>Microprobe</td>
<td>26.8 (± 0.2)</td>
<td>33.8 (± 0.2)</td>
<td>39.3 (± 0.2)</td>
</tr>
<tr>
<td>3</td>
<td>Nominal</td>
<td>50</td>
<td>40</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Microprobe</td>
<td>49.8 (± 1.0)</td>
<td>40.6 (± 0.7)</td>
<td>9.57 (± 0.3)</td>
</tr>
<tr>
<td>4</td>
<td>Nominal</td>
<td>42</td>
<td>28</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>Microprobe</td>
<td>41.4 (± 0.8)</td>
<td>29.5 (± 0.3)</td>
<td>29.1 (± 0.5)</td>
</tr>
</tbody>
</table>
inhomogeneities from top to bottom or from center to outer edge. However, the microstructural characterization of the as-received alloy samples did show inhomogeneous microstructures that were observed primarily along the thickness direction of the cast samples, i.e. from top to bottom. This inhomogeneity was most probably due to uneven solidification rates between the surface making contact with the water cooled Cu plates of the arc melter and the untouched top surface of the samples.

Due to the significant nonuniformities that were observed in the as-received microstructures, a procedure was adopted that involved re-arc melting fragments of the 200 gram samples into smaller 3 gram samples. The re-arc melting was performed at the University of Florida using a non-consumable tungsten electrode under pressurized flowing argon gas. The fragmented pieces were placed in cavities on a water cooled copper base plate and re-arc melted (RAM) a total of at least 4 times to ensure complete mixing, in case there were some chemical inhomogeneities between the fragments. The molten samples took approximately 2 to 3 seconds to solidify and reached a temperature that gave them a metallic lustre. This procedure reduced the microstructural inhomogeneities of alloys 2, 3, and 4. The compositions of the re-arc melted samples of alloys 2, 3, and 4 were analyzed by electron microprobe and are given in Table 3.1. The results obtained by the microprobe analysis for the re-arc melted alloys are close to the nominal compositions of the as-received alloys.

The interstitial oxygen and nitrogen content of the as-received alloy 2 was determined by wet chemical analysis at Teledyne Wah Chang Albany (TWCA). The
results of this analysis showed that the oxygen content was \( \sim 490 \text{ ppm} \) and the nitrogen content was \( \sim 48 \text{ ppm} \).

3.2 Heat Treatments

The heat treatment experiments were conducted with two types of furnaces depending on whether a fast or slow cooling rate was needed. The two furnaces used were a CM model 1600 vertical tube furnace and a Vacuum Industries high vacuum furnace.

The vertical tube furnace was used when fast cooling rates were needed, such as during water quenching. This furnace consisted of a mullite tube that was surrounded by MoSi\(_2\) heating elements. The mullite tube was sealed at the top and bottom with water-cooled removable fixtures. When the fixtures were closed at both ends, the tube could be pressurized slightly with a flowing stream of argon gas that entered at the top and exited at the bottom fixtures. The top fixture was designed to allow both a sample and a type B thermocouple to be positioned within the heating zone of the furnace. The thermocouple was used to monitor the temperature during the heat treatment and was also used to calibrate the heating zone. The calibration showed that the heating zone was constant to within \( \pm 5^\circ\text{C} \) over the tube length of \( \pm 6\text{cm} \) from the center of the furnace. The sample was placed on an alumina boat which was suspended in the heating zone with molybdenum or tungsten wire. The temperature difference between the sample and the thermocouple was estimated to be less than \( \pm 5^\circ\text{C} \), since the heating zone of the furnace was radially uniform due to the cylindrical design. Following is the typical experimental procedure:

1. Ramp the furnace at \( \sim 10^\circ\text{C}/\text{min} \) to the heat treatment temperature.

2. Insert the sample into the heating zone and seal the top fixture.
(3) Hold the sample under flowing argon for the duration of the heat treatment.

(4) Open the bottom fixture, cut the wire, and allow the sample to fall into the quenching media.

Water was used as the quenching media in this study in order to obtain rapid cooling rates. However, there were a few heat treatments that were performed in the vertical tube furnace in which the sample was simply dropped from the heating zone onto the bottom fixture. This permitted the samples to be air cooled, which represented a cooling rate that was intermediate between water quenching (fast) and furnace cooling (slow).

The vacuum furnace was used in experiments that needed a slow cooling rate. This furnace consisted of an alumina crucible that was surrounded by a tantalum resistive heating cage. A type R thermocouple was used to monitor the temperature and was positioned 3cm from the sample in the heating zone. The furnace incorporated a diffusion pump capped by a water baffle, so that the furnace was capable of obtaining a pressure of 1 to $4 \times 10^{-6}$ Torr depending on the heat treatment temperature. Following is the typical procedure for using the vacuum furnace:

(1) Place the sample on the alumina crucible.

(2) Place the bell jar over the sample and pump to the base vacuum pressure.

(4) Ramp the furnace to the heat treatment temperature at ~$10^\circ$C/min.

(5) Hold at the heat treatment temperature for the duration of the experiment.

(6) Turn the power off to the transformer and allow the sample to cool to room temperature inside the furnace.

(7) Vent to atmospheric pressure when the temperature, monitored by the thermocouple, is below ~$200^\circ$C.
This procedure involved a slow heating rate for the sample up to the aging temperatures since a high vacuum had to be obtained prior to heating the sample. The temperature was monitored with the thermocouple during furnace cooling and followed a parabolic curve for the heat treatments.

3.2.1 Long-Term Heat Treatment Experiments

Table 3.2 lists the long-term heat treatment conditions of samples that were used in this study. The list includes the initial cast condition, the heat treatment parameters, and the cooling method that was employed.

Most of the heat treatments that were used in this study were conducted with 3 gram RAM samples using the vertical tube furnace. These samples were heat treated in the as-cast RAM condition for 2 to 12 hours, depending on the temperature, and then water quenched. Heat treatments conducted above ~1200°C varied from 2 to 4 hours in duration while those that were conducted below this temperature were either 12 or 16 hours.

Three of the heat treatments were performed with material that was cut from the as-received 200 gram arc-melted sample of alloy 4. The three samples used in these heat treatment experiments were first heated to 1550°C for 2 hours in the vertical tube furnace and then air cooled. Further heat treatments were then conducted on two of these samples: one was heat treated at 1515°C for 2 hours and air cooled and the other was heat treated at 1000°C for 16 hours and air cooled.

There were five heat treatment experiments that were performed with the vacuum furnace. With the exception of the alloy 2 sample which was heat treated at 1200°C and furnace cooled, these experiments were designed to investigate the effect that a slow cooling rate had on the microstructures of alloys 2 and 4. The 3 gram
RAM samples were used in all of these heat treatments and all of these heat treatments lasted for a duration of 4 hours.

3.2.2 Short-Term Heat Treatment Experiments

Table 3.3 lists a set of 3 gram RAM samples that were heat treated for very short times lasting from 2 to 5 minutes. These heat treatments were conducted in the vertical tube furnace and water quenched. These heat treatments were designed to investigate the evolution of the high temperature phase equilibria.

3.3 Characterization Techniques

The microstructures of the cast and heat treated samples were investigated using optical microscopy and transmission electron microscopy (TEM) techniques. Optical microscopy was used primarily for the macroscopic characterization of the samples due to its low magnification capabilities. A Nikon microscope and Leica microscope were used in this study. The TEM was used extensively for the microscopic analysis of the samples due to its combined diffraction and image analysis capabilities while complimented with composition analysis using Energy Dispersive Spectroscopy (EDS) on a submicron microstructural scale. Three microscopes were used over the course of this investigation: a JEOL 200CX ASTEM (Analytical Scanning Transmission Electron Microscope) and a JEOL 4000FX TEM located at the University of Florida, FL and a JEOL 2000FX ASTEM located at the New York State College of Ceramics at Alfred University, NY.

The analysis of materials using the TEM has been widely employed over the past 30 years. The methods that were predominantly used in this investigation included selected area electron diffraction (SAED), convergent beam electron diffraction (CBED), and amplitude contrast image formation. The SAED analysis was
Table 3.2. Long-term heat treatments used for alloys 2 and 4.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Initial Condition</th>
<th>Temp.</th>
<th>Time</th>
<th>Cooling Method</th>
<th>Furnace Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>RAM</td>
<td>1500°C</td>
<td>2 hours</td>
<td>Water Quench</td>
<td>Tube</td>
</tr>
<tr>
<td>2</td>
<td>RAM</td>
<td>1400°C</td>
<td>4 hours</td>
<td>Water Quench</td>
<td>Tube</td>
</tr>
<tr>
<td>2</td>
<td>RAM</td>
<td>1400°C</td>
<td>4 hours</td>
<td>Furnace Cool</td>
<td>Vacuum</td>
</tr>
<tr>
<td>2</td>
<td>RAM</td>
<td>1300°C</td>
<td>4 hours</td>
<td>Water Quench</td>
<td>Tube</td>
</tr>
<tr>
<td>2</td>
<td>RAM</td>
<td>1200°C</td>
<td>4 hours</td>
<td>Furnace Cool</td>
<td>Vacuum</td>
</tr>
<tr>
<td>2</td>
<td>RAM</td>
<td>600°C</td>
<td>12 hours</td>
<td>Water Quench</td>
<td>Tube</td>
</tr>
<tr>
<td>2</td>
<td>RAM</td>
<td>400°C</td>
<td>12 hours</td>
<td>Water Quench</td>
<td>Tube</td>
</tr>
<tr>
<td>4</td>
<td>AR</td>
<td>1550°C</td>
<td>2 hours</td>
<td>Air Cool</td>
<td>Tube</td>
</tr>
<tr>
<td>4</td>
<td>AR</td>
<td>1550°C</td>
<td>1 hour</td>
<td>Water Quench</td>
<td>Tube</td>
</tr>
<tr>
<td>4</td>
<td>AR</td>
<td>1515°C</td>
<td>2 hours</td>
<td>Air Cool</td>
<td>Tube</td>
</tr>
<tr>
<td>4</td>
<td>RAM</td>
<td>1400°C</td>
<td>4 hours</td>
<td>Water Quench</td>
<td>Tube</td>
</tr>
<tr>
<td>4</td>
<td>RAM</td>
<td>1400°C</td>
<td>4 hours</td>
<td>Furnace Cool</td>
<td>Vacuum</td>
</tr>
<tr>
<td>4</td>
<td>RAM</td>
<td>1300°C</td>
<td>4 hours</td>
<td>Water Quench</td>
<td>Tube</td>
</tr>
<tr>
<td>4</td>
<td>RAM</td>
<td>1300°C</td>
<td>4 hours</td>
<td>Furnace Cool</td>
<td>Vacuum</td>
</tr>
<tr>
<td>4</td>
<td>RAM</td>
<td>1200°C</td>
<td>4 hours</td>
<td>Water Quench</td>
<td>Tube</td>
</tr>
<tr>
<td>4</td>
<td>RAM</td>
<td>1200°C</td>
<td>4 hours</td>
<td>Furnace Cool</td>
<td>Vacuum</td>
</tr>
<tr>
<td>4</td>
<td>AR</td>
<td>1000°C</td>
<td>16 hours</td>
<td>Air Cool</td>
<td>Tube</td>
</tr>
</tbody>
</table>

Note: AR - As-Received 200 gram arc-melted sample. 
RAM - Re-Arc Melted 3 gram sample. 
* - solutionized at 1550°C for 2 hours and air cooled.
### Table 3.3. Short-term heat treatments used for alloys 2 and 4.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Initial Condition</th>
<th>Temp.</th>
<th>Time</th>
<th>Cooling Method</th>
<th>Furnace Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>RAM</td>
<td>1200°C</td>
<td>2 min.</td>
<td>Water Quench</td>
<td>Tube</td>
</tr>
<tr>
<td>2</td>
<td>RAM</td>
<td>1200°C</td>
<td>5 min.</td>
<td>Water Quench</td>
<td>Tube</td>
</tr>
<tr>
<td>4</td>
<td>RAM</td>
<td>1200°C</td>
<td>2 min.</td>
<td>Water Quench</td>
<td>Tube</td>
</tr>
<tr>
<td>4</td>
<td>RAM</td>
<td>1200°C</td>
<td>5 min.</td>
<td>Water Quench</td>
<td>Tube</td>
</tr>
<tr>
<td>4</td>
<td>RAM</td>
<td>1000°C</td>
<td>2 min.</td>
<td>Water Quench</td>
<td>Tube</td>
</tr>
</tbody>
</table>
used for routine phase identification and crystallographic information, such as the analysis of twins, orientation relationships, and stacking faults. The convergent beam electron diffraction (CBED) technique was used for detailed phase analysis where symmetry information was required. This method enabled the crystal point group and the space group of the phase to be determined. These images were obtained using amplitude contrast methods based on two-beam and multiple-beam (i.e. near Laue zone axes) conditions. This method was also used to obtain either bright field or dark field images depending on the beam tilt conditions.

The SAED patterns that were used for phase identification were measured with a Starrett measuring table. This instrument permitted both linear and angular measurements to be made with accuracies of ±0.025mm for linear measurements and ±0.083° for angular measurements.

3.4 Sample Preparation

3.4.1 Optical Microscopy

The sample preparation that was used for optical microscopy consisted of standard metallographic methods. The 3 gram RAM samples were mechanically sectioned into 0.5 to 1.0mm thick samples using a diamond edged cutting wheel. These samples were then mounted in 1in diameter molds using phenolic powder. A polished surface of 0.03µm was obtained using standard grinding and polishing methods. The grinding steps were done using 240 to 600 grit SiC paper. The polishing steps were performed with Al₂O₃ powder on appropriate cloths. Finally, the samples were etched using Kroll's etchant.
3.4.2 Transmission Electron Microscopy

The sample preparation for TEM used the jet-polishing method. This method consisted of a mechanical preparation step and an electro-chemical polishing step.

The mechanical preparation step involved cutting a wafer from the bulk sample, cutting a 3mm diameter disc from the wafer, and finally reducing the thickness of the 3mm disc to about 0.2mm (200µm). The starting bulk sample was either a 3 gram RAM sample or roughly a 1cm × 1cm × 1cm as-received (AR) sample. Care was taken in this procedure to select TEM samples that were representative of the bulk sample. In general, wafers that were cut near the mid-section of the bulk sample were selected for the next step of obtaining the 3mm disc. It was necessary to obtain the 3mm disc from the center of the wafer in order to avoid the heat affected zone (HAV) that was observed by optical microscopy in several heat treated samples. The method that was employed in obtaining the 3mm disc was different than that which is customarily used, since the heat treated samples often fractured in a brittle manner during the preparation when using the hole punch or the ultrasonic disc cutter. The alternative procedure consisted of mounting the wafer using superglue on the end of a ~2.8mm diameter stainless steel rod. The edges of the wafer were then smoothed down by mechanical grinding on 600 grit SiC paper until a circular 3mm disc was obtained. After obtaining the 3mm disc, the thickness was then reduced by mechanical grinding methods to a thickness of ~200 to 300µm using SiC grit paper.

The electro-chemical polishing step used the jet-polishing technique in order to obtain an electron transparent region near the center of the 3mm disc sample. This procedure was conducted with a Struers Tenupol jet-polisher and an electrolytic solution. The electrolyte that gave the best polishing results was based on
4%Hf + 10%H₂SO₄ + 86%Methanol. The following polishing parameters gave consistently good results: -50°C to -40°C temperature range, 25 volts DC, and moderate to low flow rate. After a hole developed in the sample, the sample was quickly removed from the polisher and rinsed in two successive methanol baths.
CHAPTER 4
EQUILIBRIUM PHASE TRANSFORMATION STUDY

4.1 Introduction

The literature review in Chapter 2 indicated the complexity of the phase equilibria in the Nb-Ti-Al system. As was previously stated, the foremost reason for the complexity of this system is that there are a multitude of equilibrium binary phases and at least two ternary phases which exist in this ternary system. This combined with the fact that the solidus temperature over most of the ternary system lies above \( \approx 1500°C \), means that most of the comprehensive phase equilibria studies have concentrated on one or two temperatures for heat treatments. The most common temperature has been \( 1200°C \). A further complication is that a number of metastable phases, such as the martensitic \( \alpha' \), \( \alpha'' \), and \( \omega \)-related phases, form in competition with the equilibrium phases in this system. The presence of these metastable phases can complicate the development of the equilibrium microstructures and may cause confusion in the equilibrium phase analysis.

Therefore, the purpose of chapter 4 is two-fold: to determine the equilibrium phases and to describe their development into the equilibrium microstructures in alloys 2 and 4. The as-cast microstructure of a third alloy (alloy 3) with a composition of 50Nb-40Ti-10Al (at.%) was investigated in order to compare properties of the BCC \( \beta \) phase to that of alloys 2 and 4. This background information on the \( \beta \) phase will then provide the basis for investigation of the metastable phases in chapters 5 and 6.
The results of this chapter are divided into three sections: (1) the as-cast, (2) the long-term heat treatment, and (3) the short-term heat treatment microstructures. Using these results, the discussion of this chapter is then divided into three main parts: (1) high temperature $\beta$-phase, (2) equilibrium microstructures at the aging temperatures, and (3) equilibrium phase transformation mechanisms.

4.2 Results

4.2.1 As-Cast Microstructures

The analysis of as-cast microstructures consisted of re-arc melted (RAM) samples of alloys 2, 3, and 4. The cooling rate associated with these samples was relatively fast due to their small size which minimized inhomogeneous microstructures in the RAM samples. However, the RAM sample of alloy 2 showed a microstructure with an inhomogeneous distribution of precipitates. Therefore, a RAM sample of alloy 2 was also analyzed which was electromagnetically (EM) levitated and drop quenched in order to suppress the solid-state precipitation by rapid solidification.

4.2.1.1 Re-arc Melted

The as-cast microstructures that were observed in the RAM samples of alloys 2, 3, and 4 are shown in Figure 4.1. These microstructures consisted of large primary grains with a coarse dendritic structure. The size of the primary grains was typically $>300\mu$m (0.3mm). In alloy 2, an inhomogeneous distribution of acicular precipitates was observed near the grain boundaries and within the interdendritic regions (Figure 4.1a). Alloy 4 (Figure 4.1c) occasionally showed a second phase at the grain boundaries, however, alloy 3 (Figure 4.1b) showed no additional phases.
Figure 4.1. Optical micrographs showing the as-cast microstructures. (a) alloy 2; (b) alloy 3; (continued)
Figure 4.1. (continued) (c) alloy 4.
4.2.1.1.1 The Primary Phase

The primary phase in the RAM samples of alloys 2, 3, and 4 was examined by TEM and was determined to have the BCC structure, known as the β phase. Selected area electron diffraction (SAED) patterns showing the [001]β zone axis from the β matrix in each alloy are shown in Figure 4.2. The patterns show diffraction spots at the {100} positions for alloys 2 and 4 (Figures 4.2a and 4.2c, respectively); however, the one for alloy 3 does not show these spots (Figure 4.2b). The {100} spots denote that the β phase in alloys 2 and 4 has an ordered BCC structure, or B2 (CsCl) structure, and are referred to as superlattice reflections. The fact that no superlattice reflections are observed in alloy 3 indicates that the β phase has a disordered structure.

Micrographs that were obtained using a two-beam condition with a (100)β superlattice reflection are shown in Figure 4.3. These micrographs show the presence of large anti-phase domain boundaries (APDBs) in the matrix of alloys 2 and 4. The APDBs are formed during a disorder to order transition and indicate that ordering occurred during solid state cooling.

The B2 phase that was observed in alloys 2 and 4 exhibited several diffuse scattering anomalies. The results showing these anomalies are grouped into three categories: diffuse streaking, splitting of diffraction spots, and localized diffuse intensity maxima. A tweed structure that correlated with the diffuse streaking and spot splitting was also observed.

The diffuse streaking and the splitting of diffraction spots are best observed at the [001]β zone axis, as shown in Figure 4.2a for alloy 2 and 4.2c for alloy 4. The streaking was continuous in the <110> directions and intersected both fundamental
Figure 4.2. SAED patterns showing the [001] zone axis of the β matrix. (a) alloy 2; (b) alloy 3; (continued)
Figure 4.2. (continued) (c) alloy 4.
Figure 4.3. TEM micrographs showing the APDBs in the B2 matrix. (a) alloy 2; (b) alloy 4.
and superlattice reflections. The splitting of diffraction spots was observed as satellite reflections that were displaced from the reciprocal lattice position in <100> directions. The separation of the split reflections increased as the order of reflection increased. This is demonstrated in Figure 4.4 using a SAED pattern that was tilted off the [001]ₜ zone axis along the g=(110) reflection. Splitting is observed for reflections along both the [100] and [010] directions and is greater for the (400) spot as compared to the (200) spot. Also, notice that for the (220) spot there are four satellite reflections. These are comprised of two pairs of reflections that are split along orthogonal [100] and [010] directions.

The diffuse electron scattering is best observed in SAED patterns of the <110>ₜ and <111>ₜ zone axes, as shown in Figure 4.5. The scattering consists of localized segments of diffuse intensity that extend in <112> or <110> directions and have a maxima located between the BCC diffraction spots at fractional coordinates. The diffuse intensity is superimposed on the continuous streaking that is also observed in the <112> and <110> directions. The fractional coordinates for intensity maxima in alloy 2 were at ½<110>, ½<110>, ½<112>, ½<112>, and ½<111> positions in the <110>ₜ zone axis (Figure 4.5a) and at ½<110> and ½<112> positions in the <111>ₜ zone axis (Figure 4.5b). The intensity maxima positions observed in alloy 4 were the same as those observed in alloy 2, with the exception of the ½<110> positions that were not observed at either the <110>ₜ zone axis (Figure 4.5c) or the <111>ₜ zone axis (Figure 4.5d).

The tweed structure consisted of striations that lied parallel to {110} traces of the ordered β phase, as shown in Figure 4.6. The micrograph was obtained near the [001]ₜ zone axis to show the tweed striations along two orthogonal (110) and (1T0)
Figure 4.4. SAED pattern from the B2 matrix showing the splitting of diffraction spots. The specimen was tilted away from the [001] zone axis along $g=(110)$. 
Figure 4.5. SAED patterns showing the diffuse electron scattering observed in the B2 matrix of alloy 2 (a and b) and alloy 4 (c and d). (a) [110] zone axis; (b) [111] zone axis; (continued)
Figure 4.5. (continued) (c) [110] zone axis; (d) [111] zone axis.
Figure 4.6. TEM micrographs showing the tweed microstructure in the B2 matrix.
planes. The image characteristics of the tweed structure was investigated using two-beam amplitude contrast conditions, and was found to obey the $g \cdot R = 0$ invisibility criterion (where $g$ is the reflection vector and $R$ is a general description of a displacement vector) and to depend on the deviation parameter, $s$. For example, a two-beam condition using $g = (100)$ caused both (110) and (1T0) striations to be visible, but using $g = (110)$ caused only the (110) striation to be visible. The (1T0) striations are invisible using $g = (110)$ since $g \cdot R = 0$, assuming $R = (1T0)$. Likewise, the deviation parameter, $s$, affected the tweed image, causing it to have a coarse appearance for a small $s$ magnitude and a fine appearance for a large $s$ magnitude.

4.2.1.1.2 The Precipitates in Alloy 2

The inhomogeneous distribution of precipitates observed in the as-cast microstructure of alloy 2 were divided into three representative areas: the in-matrix, the grain boundary, and the interdendritic regions. The primary difference between the in-matrix and the interdendritic regions was the presence of acicular shaped precipitates which were observed by optical microscopy, as seen in Figure 4.1.

The in-matrix region consisted of a high number density of very small precipitates, as can be seen in Figure 4.3b. The precipitates were homogeneously distributed within the matrix and yet were not affected by the APDBs that had formed during the $\beta$ phase disorder/order transition. The analysis of the small precipitates identified them as being related to the class of $\omega$-phases, a close-packed hexagonal structure [58] which will be discussed further in chapter 5.

A TEM micrograph of the grain boundary region is shown in Figure 4.7. This region consisted of B2 grains with the $\gamma$ phase, based on the $L1_0$ tetragonal structure with TiAl stoichiometry, distributed along the grain boundaries. Two morphologies
were observed for the γ grains: a blocky type that formed along the B2 grain boundaries and a lath type that extended from the blocky grains into the B2 matrix. The formation of Widmanstätten laths from grain boundary allotriomorphs [80] resembles this type of microstructure. The laths were observed to have an orientation relationship with the B2 matrix which was determined to be as follows:

\[ <110>_{\gamma} \parallel <111>_{\beta} \quad \text{and} \quad \{1\overline{1}1\}_{\gamma} \parallel \{1\overline{1}0\}_{\beta} \]

and is shown in the SAED pattern in Figure 4.7b. The grain boundary allotriomorphs contained stacking faults that formed on the \{111\} planes.

Micrographs that are representative of the interdendritic regions are shown in Figure 4.8. These regions consisted of B2 matrix with large acicular shaped precipitates as well as small in-matrix \(\omega\) precipitates. The analysis of the acicular shaped precipitates showed that they were plates and that they had an orthorhombic structure (referred to from this point on as plates). Their size was typically observed to be >10\(\mu\)m in length (l) and <0.5\(\mu\)m in thickness (t), giving them an aspect ratio >20(l/t). The small \(\omega\) precipitates were observed to be homogeneously distributed about the plates. However, occasionally large \(\omega\) precipitates were observed in contact with the plates, as shown in Figure 4.8b. A detailed analysis of the plates will be covered in chapter 6.

4.2.1.2 EM Levitated and Drop Quenched

The levitated and drop quenched sample of alloy 2 was found to consist of an acicular microstructure, as shown in Figure 4.9. The optical micrograph in Figure 4.9a showed that the microstructure had a basket weave appearance. The TEM micrograph in Figure 4.9b revealed that a high number density of lenticular-shaped plates had formed in the ordered \(\beta\) matrix. The ordered \(\beta\) matrix was also found to
Figure 4.7. Shows the microstructure of the as-cast sample of alloy 2. (a) TEM micrograph showing the grain boundary allotriomorphs and Widmanstatten laths of the $\gamma$-TiAl phase; (b) SAED pattern showing the orientation relationship observed between the $\gamma$ laths and B2 matrix, which was $<110>_{\gamma} \parallel <111>_{\beta}$ and $\{111\}_{\gamma} \parallel \{110\}_{\beta}$. 
Figure 4.8. TEM micrographs of the B2 matrix in the as-cast sample of alloy 2. (a) the small ε-related precipitates and lenticular-shaped plates; (b) the coarse ε-related precipitates adjacent to the plate.
Figure 4.9. Shows the acicular microstructure observed in the EM-levitated and drop quenched sample of alloy 2. (a) Optical micrograph; (b) TEM micrograph.
have contained APDBs. The analysis of these plates showed that they were the same as those that were observed in Figure 4.8 for the RAM sample.

4.2.2 Long-Term Heat Treatments

4.2.2.1 Analysis of Alloy 2

The long-term heat treatments used for alloy 2 were shown in Table 3.2. The 1500°C heat treatment lasted 2 hours while the 1400°C, 1300°C, and 1200°C heat treatments were for a duration of 4 hours. All of the heat treatments used a water quench to cool the samples to room temperature except for the 1200°C treatment which used a furnace cool.

4.2.2.1.1 Optical Microscopy

Micrographs that are representative of the microstructures observed in samples aged at 1300°C, 1400°C, and 1500°C and subsequently water quenched are shown in Figure 4.10. Note that the microstructures do not show any evidence of the prior dendritic structure and that the heat treatments applied were sufficient to remove chemical inhomogeneities.

The microstructures of the samples aged above 1300°C all showed a matrix that resembled the acicular microstructure observed in the interdendritic regions of the as-cast sample. These microstructures showed basket weave morphologies, as shown in Figures 4.10a to 4.10c. The grain boundaries observed in these microstructures indicated that the matrix consisted of a single phase at high temperatures and had a grain size of 1 to 2 mm. The entire microstructures of 1400°C and 1500°C aged samples consisted of the acicular microstructure. However, the sample aged at 1300°C also showed large blocky-shaped second phase particles that formed within the matrix and at grain boundaries. A two-phase microstructure was
Figure 4.10. Optical micrographs showing the microstructures of the long-term thermally aged samples of alloy 2. (a) 1500°C-4hrs-WQ; (b) 1400°C-4hrs-WQ; (continued)
Figure 4.10. (continued) (c) 1300°C-4hrs-WQ; (d) 1200°C-4hrs-FC.
also observed in the sample aged at 1200°C and furnace cooled and is shown in Figure 4.10d.

4.2.2.1.2 Microprobe Analysis

The results of the microprobe analysis on the samples that were heat treated at 1400°C, 1300°C, and 1200°C are shown in Table 4.1. This table showed that the σ phase, which has the binary Nb₂Al stoichiometry, has a large solubility range for Ti. The σ phase was determined to contain ≈26%Ti at 1300°C and ≈30%Ti (at.%) at 1200°C. The Al content was not found to have changed appreciably in the σ phase that was present at these temperatures. Therefore, the stoichiometry of the σ phase remained close to the ratio of (Nb+Ti)₂Al. Similarly, the γ phase, which has the binary TiAl stoichiometry, was determined to have a large solubility range for Nb that was found to be ≈21at.%Nb. The Al content of the γ phase was found to be ≈43at.%Al which was low compared to the composition of the binary TiAl phase.

4.2.2.1.3 Transmission Electron Microscopy

The general appearances of the microstructures observed by TEM in samples aged at 1500°C, 1400°C and 1300°C and then water quenched are shown in Figure 4.11. A common observation made for all three heat treatments was that the matrix contained a large number density of plates. The matrix was identified as the ordered β (B2) phase. APBDs were observed and were consistently smaller in the aged samples as compared to the as-cast sample. Assuming that the APDBs formed upon cooling, the smaller size was most probably due to the solid-state cooling rate which was faster in the aged samples because of the water quenching. The analysis of the plates determined that they were similar to those that were observed in the as-cast sample (see Figure 4.8).
Table 4.1. Microprobe results of the aged samples of alloy 2.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Phase</th>
<th>Nb (at.%)</th>
<th>Ti (at.%)</th>
<th>Al (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1400°C</td>
<td>β</td>
<td>26.83 (± 0.19)</td>
<td>33.85 (± 0.18)</td>
<td>39.32 (± 0.17)</td>
</tr>
<tr>
<td>1300°C</td>
<td>β</td>
<td>23.06 (± 0.06)</td>
<td>36.90 (± 0.07)</td>
<td>40.4 (± 0.11)</td>
</tr>
<tr>
<td></td>
<td>σ</td>
<td>36.39 (± 0.18)</td>
<td>26.35 (± 0.15)</td>
<td>37.26 (± 0.24)</td>
</tr>
<tr>
<td>1200°C</td>
<td>σ</td>
<td>34.06 (± 0.80)</td>
<td>29.85 (± 0.41)</td>
<td>36.10 (± 0.42)</td>
</tr>
<tr>
<td></td>
<td>γ</td>
<td>20.71 (± 2.39)</td>
<td>36.56 (± 1.53)</td>
<td>42.73 (± 1.22)</td>
</tr>
</tbody>
</table>
Figure 4.11. TEM micrographs showing the microstructures of the long-term thermally aged samples of alloy 2. (a) 1400°C-4hrs-WQ; (b) 1300°C-4hrs-WQ.
The large particles in the two-phase microstructure of the sample aged at 1300°C were identified as the \( \sigma \)-(Nb\(_2\)Al + Ti) phase and are shown in Figure 4.11b. The \( \sigma \) phase was determined by SAED analysis to have a tetragonal unit cell with lattice parameters of \( a = 9.92\) Å and \( c = 5.17\) Å (± 0.05 Å). These results are consistent with the \( \sigma \) phase that forms in a variety of transition metal alloy systems [39]. The \( \sigma \) phase has been shown to be a complex tetragonal structure containing 30 atoms and possessing some degree of order between 5 distinct crystallographic sites [39,41]. The following characteristics of the \( \sigma \) grains were determined from this analysis: (1) a grain size of up to 10-15\( \mu \)m; (2) a low number density of stacking faults on (100), (010), and (110) planes; and (3) the presence of low angle grain boundaries.

The two-phase microstructure of the sample aged at 1200°C and furnace cooled is shown in Figure 4.12. The grains that have light contrast in these micrographs were identified from the SAED analysis to be the \( \gamma \) phase while the grains that have dark contrast were identified to be the \( \sigma \) phase. The \( \gamma \) phase was observed to have a lath morphology and was surrounded by a continuously connected matrix that was the \( \sigma \) phase. A longitudinal view of the \( \gamma \) phase laths is shown in Figure 4.12a and a transverse view of them is shown in Figure 4.12b. Figure 4.12a shows that each lath consisted of a colony of small grains of the same phase. The grain size of each phase was observed to be less than ~3\( \mu \)m. Annealing twins were observed in many of the \( \gamma \) grains and can be seen in the normal orientation. The twin system was determined to be \( \langle 112 \rangle \{111\} \) which was the same as that reported for mechanical twins in the \( \gamma \) phase [81].

A diffraction study was performed on the \( \gamma \) phase to determine the site occupancy of Nb in the unit cell since the microprobe results in Table 4.1 showed that
it contained up to ~21at.%Nb. The results from the diffraction study are shown in Figure 4.13. The analysis of the two diffraction patterns showed that the (110) and (001) spots were observed at the [110] zone axis (Figure 4.13a), but that the (010) and (001) spots were absent at the [101] zone axis (Figure 4.13b). The structure factor rule for diffraction in the binary TiAl structure predicts that diffraction is forbidden and will not be observed when (h+k)=odd. Since the h+k sum is odd for the (101) and (010) reflections and is even (zero is included) for the (110) and (001), then these results are consistent with the structure factor of the binary γ TiAl phase. Thus, this indicates that Nb randomly occupies the Ti sites in the γ phase of alloy 2.

Table 4.2 contains a summary of the results obtained by TEM for the heat treated samples of alloy 2. It includes the phases that were observed and a brief comment about each.

4.2.2.2 Analysis of Alloy 4

Heat treatments that lasted from 2 to 16 hours with a variety of different cooling methods were used on alloy 4. The following are the heat treatment parameters for alloy 4 samples from Table 3.2: (1) two heat treatments at 1550°C and 1515°C for 2 hours with air cooling; (2) four heat treatments which included one at 1550°C for 2 hours and three at 1400°C, 1300°C, and 1200°C for 4 hours with water quenching; (3) three heat treatments at 1400°C, 1300°C, and 1200°C for 4 hours with furnace cooling; (4) one heat treatment at 1000°C for 16 hours with air cooling; and (5) two heat treatments at 600°C and 400°C for 12 hours with water quenching.

4.2.2.2.1 Optical Microscopy

The typical microstructures of samples that were heat treated at high temperatures are shown in Figure 4.14. The prior dendritic structure of the as-cast
Figure 4.12. TEM micrographs showing the $\gamma$ laths in the $\sigma + \gamma$ microstructure of the thermally aged 1200°C-4hrs-FC sample of alloy 2. (a) longitudinal view; (b) transverse view.
Figure 4.13. SAED patterns of the $\gamma$ phase observed in the 1200°C-4hrs-FC sample of alloy 2. (a) the [110], zone axis; (b) the [101], zone axis.
Table 4.2. Summary of the phases identified by TEM in the aged samples of alloy 2.

<table>
<thead>
<tr>
<th>Heat Treatment</th>
<th>Phases Present</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1500°C-2hrs-WQ</td>
<td>B2 + plates</td>
<td>APBDs and plates present in the B2 matrix.</td>
</tr>
<tr>
<td>1400°C-4hrs-WQ</td>
<td>B2 + plates</td>
<td>APBDs and plates present in the B2 matrix.</td>
</tr>
<tr>
<td>1300°C-4hrs-WQ</td>
<td>B2 + σ + plates</td>
<td>APBDs and plates present in the B2 matrix and large σ grain size.</td>
</tr>
<tr>
<td>1200°C-4hrs-FC</td>
<td>σ + γ</td>
<td>Lath structure and small σ and γ grain sizes.</td>
</tr>
</tbody>
</table>
sample was not observed in any of the aged samples with the exception of the 1200°C sample.

The optical micrographs showed microstructures that evolved from precipitation of a second phase from the primary single phase that was stable at high temperatures. Above 1550°C (Figure 4.14a), the microstructure consisted of single phase grains that had a grain size of 1 to 2mm, straight grain boundaries, and triple points. Between 1515°C and 1550°C (Figure 4.14b), a second phase formed as blocky particles (idiomorphs) within the matrix and at the grain boundaries of the matrix. This second phase increased in volume fraction at lower temperatures and below 1300°C was observed as the matrix, i.e. the phase with the larger volume fraction (Figures 4.14c to 4.14f). In the samples aged at 1300°C and 1200°C the retained primary phase appeared as an irregular, circular, and elongated morphology, as can be seen in Figures 4.14d and 4.14e. The two-phase microstructure observed in the sample aged at 1000°C is shown in Figure 4.14f. The morphology of these second phase particles from Figure 4.14f was mostly of a circular shape and the size was typically less than 1µm.

4.2.2.2.2 Transmission Electron Microscopy

The microstructure of the sample aged at 1550°C and water quenched was found to consist of the B2 matrix. As shown in Figure 4.15, the B2 matrix consisted of APDBs that were smaller than those observed in the RAM sample of Figure 4.3c. The presence of these APDBs indicated that the matrix consisted of the disordered β phase at the 1550°C aging temperature.

Below 1550°C, the σ phase was observed to have nucleated from the β phase to form a two-phase microstructure. This was determined from the analysis of the
Figure 4.14. Optical micrographs showing the microstructures of the long-term thermally aged samples of alloy 4. (a) 1550°C-2hrs-AC; (b) 1515°C-2hrs-AC; (continued)
Figure 4.14. (continued) (c) 1400°C-4hrs-WQ; (d) 1300°C-4hrs-WQ; (continued)
Figure 4.14. (continued) (e) 1200°C-4hrs-WQ; (f) 1000°C-16hrs-AC.
Figure 4.15. TEM micrograph showing the APDBs in the B2 matrix of the sample from alloy 4 that was heat treated at 1550°C and water quenched.
samples heat treated at 1400°C, 1300°C, and 1200°C and subsequently water quenched. The σ grains were between 5 and 15µm in size and were typically isolated in the β matrix at 1400°C, but formed a matrix of connected σ grains below 1300°C. The β phase in these microstructures possessed the B2 structure and contained small APDBs in all of the heat treated samples. It also exhibited the same type of image and diffraction characteristics that have been previously documented for the B2 phase. The irregular, elongated, and circular morphologies of the B2 phase which were recognized by optical microscopy could be identified clearly in the TEM, as shown in Figure 4.16. This irregularly shaped B2 phase was located primarily at σ grain boundaries. In general, the irregularly shaped B2 particles were retained β which had formed isolated grains due to the growth and impingement of σ grains with one another. This type of morphology was observed mostly at aging temperatures greater than 1300°C. The circular and elongated cross-sections arose from the rod-shaped morphology of the B2 phase which was commonly observed at aging temperatures below 1300°C.

The effect of cooling rate on the microstructures was studied using the same heat treatments at 1550°C, 1400°C, 1300°C, and 1200°C, but with either air cooling or furnace cooling. It was found from these heat treatments that the stability of the high temperature β phase to the solid state phase transformations depended on the cooling rate.

The 1550°C aged sample was air cooled and was found to consist of an inhomogeneous distribution of small precipitates in the B2 matrix as shown in Figure 4.17. The analysis of the B2 matrix revealed large APDBs, a tweed structure, and the same general characteristics that were observed for the B2 phase found in the
Figure 4.16. TEM micrographs showing the different morphologies of the retained $\beta$ phase observed in the samples of alloy 4 that were heat treated at 1200°C, 1300°C, and 1400°C and water quenched. (a) the irregular and circular morphologies; (b) the elongated morphology.
Figure 4.17. TEM micrograph showing the precipitates of the orthorhombic phase that formed on the APDBs and in the B2 matrix of alloy 4 during air cooling from 1550°C.
as-cast microstructure. The precipitates were observed to have formed both on the APDBs and within the domains of the APDBs. A denuded zone, or region that contained no precipitates, was observed adjacent to the APDBs.

The analysis of the precipitates that formed in the B2 matrix during air cooling showed them to be consistent with the orthorhombic phase, which was based on the Ti$_2$AlNb stoichiometry [13]. In Figure 4.18, the SAED analysis showed that the orthorhombic precipitates formed from the β phase with the following orientation relationship:

\[ [110]_β \parallel [001]_0 \quad \text{and} \quad (112)_β \parallel (110)_0. \]

The a, b, and c lattice parameters of the orthorhombic phase were calculated from electron diffraction patterns and were \( a_0 = 6.13\text{Å} \ (± 0.07\text{Å}) \), \( b_0 = 9.35\text{Å} \ (± 0.11\text{Å}) \), and \( c_0 = 4.57\text{Å} \ (± 0.06\text{Å}) \). The calculated lattice parameter of the ordered β phase in the 1550°C aged sample was \( a_β = 3.23\text{Å} \ (± 0.03\text{Å}) \). The c-axis lattice parameter of the orthorhombic phase was determined to be related to the a-axis lattice parameter of the B2 phase by \( c_0 = \sqrt{2}a_β. \)

The samples that were aged at 1400°C, 1300°C, and 1200°C and furnace cooled showed the same two-phase σ + β microstructures that were observed in the water quenched samples. However, the furnace cooled samples showed microstructures that also contained the orthorhombic phase. The analysis showed that the orthorhombic phase formed from the ordered β phase with the same orientation relationship that was previously shown. The analysis of the particles with the B2 phase did not reveal any APDBs, but it was determined that the APDBs had nucleated and grown to the size of the particles during furnace cooling. The analysis also showed that the orthorhombic phase had a plate morphology and formed at the
Figure 4.18. SAED pattern showing the orientation relationship between the orthorhombic phase and the B2 phase in the 1550°C-2hrs-AC sample of alloy 4. The OR was consistent with [001]_O ̂= [110]_B and (110)_O ̂= {112}_B.
\( \sigma/\beta \) interface as shown in Figure 4.19. The plates were observed to have contained a low number density of stacking faults that were parallel to the \((001)_{o}\) planes. An attempt was made to observe the domain structure in the orthorhombic plates using dark field imaging techniques, however, this study showed that there were no APDBs present in these plates. The habit plane of the plates was determined at the \([001]_{o}\) zone axis and was found to lie \(-9^\circ\) from the \((211)_{\beta}\) planes of the \(\beta\) matrix. There was no apparent dislocation structure at the interface between the plates and the \(\beta\) phase, which was examined using conventional diffraction contrast imaging techniques.

The sample that was aged at 1000\(^\circ\)C and air cooled showed a two-phase microstructure that consisted of the \(\sigma\) and orthorhombic phases. The matrix was composed of large \(\sigma\) grains with small particles of the orthorhombic phase at the \(\sigma\) grain boundaries and is shown in Figure 4.20. The SAED pattern in Figure 4.20b shows the \((110)_{o}\) zone axis of the orthorhombic phase.

The investigation of the \(\sigma\) matrix in the 1000\(^\circ\)C and 1200\(^\circ\)C aged samples revealed large colonies that consisted of multiple \(\sigma\) grains with similar orientations. Evidence of this is shown in Figure 4.21 by tilting a single \(\sigma\) grain to the \([001]_{\sigma}\) zone axis. It was also observed that when this zone axis was reached many of the surrounding \(\sigma\) grains were also oriented close to subsequent \([001]_{\sigma}\) zone axes. This is shown in the micrograph of Figure 4.21a as a collection of \(\sigma\) grains that all have a dark contrast associated with them. The dark contrast is generated by amplitude contrast conditions and signifies that all of the dark grains are oriented for strong diffraction, i.e. oriented close to a laue zone axis. This condition was also verified by using a large selected area aperture that sampled several \(\sigma\) grains and is shown in
Figure 4.19. TEM micrograph showing the orthorhombic plates that formed in the retained B2 phase of alloy 4 during furnace cooling from the heat treatment temperatures of 1200°C, 1300°C, and 1400°C.
Figure 4.20. Shows the microstructure observed in the 1000°C-16hrs-AC sample of alloy 4. (a) TEM micrograph showing particles of the orthorhombic phase observed at the grain boundaries of the σ phase; (b) SAED pattern showing the [110]_o zone axis of the orthorhombic phase.
Figure 4.21. Shows the microstructure observed in the samples of alloy 4 that were heat treated at 1000°C and 1200°C. (a) TEM micrograph showing the colony of σ grains; (b) SAED pattern showing multiple [001]$_\sigma$ zone axes from the σ grains present in the colony.
Figure 4.21b. This diffraction pattern shows several $[001]_\sigma$ zone axes from each $\sigma$ grain. Note that these are both slightly tilted and rotated from one another.

A summary of the TEM results for the long term heat treated samples of alloy 4 is given in Table 4.3. It includes a list of the phases that were present in the microstructures and a brief comment about each at the aging temperatures.

4.2.3 Short-Term Heat Treatments

These heat treatments included experiments that lasted a duration of 2 or 5 minutes and then the samples were immediately water quenched. The temperature, time, and cooling method employed for the heat treatments were shown in Table 3.3. The purpose of these experiments was to understand the mechanisms of these phase transformations that led to the formation of the two-phase microstructures in alloys 2 and 4.

4.2.3.1 Alloy 2

The samples aged at 1200°C for 2 and 5 minutes consisted of two-phase $\sigma + \gamma$ microstructures. Even in 2 minutes, the $\beta$ phase of the as-cast sample had completely transformed as shown in Figure 4.22. The transformed microstructure near a prior $\beta$ grain boundary is shown in Figure 4.22a. This figure shows that the $\gamma$ grains can generally be distinguished from the $\sigma$ grains due to a lighter contrast from a lower mass contrast. Therefore, the line of $\gamma$ grains observed with light contrast indicated that they either formed along the prior $\beta$ grain boundaries during the heat treatment or were present prior to the heat treatment. The latter may be possible since $\gamma$ grains were observed at primary $\beta$ grain boundaries in the as-cast microstructure as was shown in Figure 4.7. Figure 4.22b shows a $\sigma$ grain that was purposely tilted to the $[110]_\sigma$ orientation in order to exhibit strong diffraction contrast. This produced a
Table 4.3. Summary of the phases identified by TEM in the aged samples of alloy 4.

<table>
<thead>
<tr>
<th>Heat Treatment</th>
<th>Phases Present</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1550°C-2hrs-WQ</td>
<td>B2</td>
<td>APDBs present in the B2 matrix.</td>
</tr>
<tr>
<td>1400°C-4hrs-WQ</td>
<td>σ + B2</td>
<td>Large σ grain size and APBDs present in the B2 particles.</td>
</tr>
<tr>
<td>1400°C-4hrs-FC</td>
<td>σ + B2 + O</td>
<td>Orthorhombic plates formed at the interface between the B2 and σ phases.</td>
</tr>
<tr>
<td>1300°C-4hrs-WQ</td>
<td>σ + B2</td>
<td>Lamellar structure and APDBs present in the B2 particles.</td>
</tr>
<tr>
<td>1300°C-4hrs-FC</td>
<td>σ + B2 + O</td>
<td>Orthorhombic plates formed at the interface between the B2 and σ phases.</td>
</tr>
<tr>
<td>1200°C-4hrs-WQ</td>
<td>σ + B2</td>
<td>Lamellar structure and APDBs present in the B2 particles.</td>
</tr>
<tr>
<td>1200°C-4hrs-FC</td>
<td>σ + B2 + O</td>
<td>Orthorhombic plates formed at the interface between the B2 and σ phases.</td>
</tr>
<tr>
<td>1000°C-16hrs-AC</td>
<td>σ + O</td>
<td>Large σ grain size with small particles of the orthorhombic phase.</td>
</tr>
</tbody>
</table>
dark contrast for the \( \sigma \) grain which demonstrated that the grain size of the \( \sigma \) phase was larger than ~5\( \mu \)m. This was larger than the grain size of the \( \gamma \) phase which was determined to be in the 0.2 to 1.0\( \mu \)m size range.

A significant difference in the morphology of the \( \sigma + \gamma \) microstructures was observed between the short-term and long-term heat treatments. The short-term heat treatment produced essentially isotropic grains of both \( \sigma \) and \( \gamma \) phases as shown in Figure 4.22. This morphology was different from that of the long-term heat treatment which produced laths consisting of rows of \( \sigma \) and \( \gamma \) grains. This long-term heat treatment morphology was previously shown by optical microscopy in Figure 4.10d and by TEM in Figure 4.12. The view that was normal to the \( \sigma + \gamma \) lath microstructure in Figure 4.12b resembled that which was observed in the short-term heat treatment. The different lath morphologies were most probably related to different heating rates, since the long-term heat treatment employed the vacuum furnace and the short-term heat treatments were conducted in the vertical tube furnace. The samples heated in the vacuum furnace were pumped to the operating vacuum pressure before the furnace was ramped up to the aging temperature. The samples heated in the tube furnace were simply dropped into the heating zone. Thus, the samples heated in the vacuum furnace experienced a slower heating rate, while the samples heated in the tube furnace experienced a faster heating rate.

**4.2.3.2 Alloy 4**

The analysis of the samples heat treated at 1200°C for 2 and 5 minutes revealed that the as-cast microstructure transformed completely to a two-phase \( \sigma + \beta \) microstructure. Figure 4.23 shows the microstructure as observed by optical microscopy using bright field and dark field conditions. TEM micrographs shown in
Figure 4.22. TEM micrographs showing the microstructure observed in the 1200°C-2min-WQ sample of alloy 2. (a) the σ (dark) and the γ (light) phases at a low magnification; (b) the σ grain size.
Figure 4.24 demonstrate that the interconnected phase is σ and the elongated lath-shape phase is disordered β phase. The sample shown in the micrographs was tilted so that a single β grain was oriented on the [001] zone axis. This subsequently caused all of the β grains to be oriented on the [001] zone axis and is observed in Figure 4.24a by the fact that all of the β grains have the same dark contrast. The sample was then tilted such that the two σ grains were oriented on the [001] zone axis. This difference in tilting amounted to a misorientation of about 13°-16° from the [001] zone axis of the β grains. This procedure caused each of the σ grains to show a dark contrast and demonstrated that each grain was greater than 10-15µm in size and contained a number of small β grains. It should also be mentioned that the β grains were observed to have an ordered structure and to contain small APBDs.

The sample that was heat treated at 1000°C for 2 minutes was observed to have a partially transformed microstructure as shown in the optical micrograph of Figure 4.25. This micrograph indicates that the transformed product forms in colonies and that nucleation occurs at the primary β grain boundaries. The TEM analysis indicated that the microstructure evolved by the cooperative formation of the two phases. A micrograph illustrating this process at the reaction front of a colony is shown in Figure 4.26. This orientation shows that the colony consisted of a rod-shape secondary β phase located between the σ phase. It was determined by SAED analysis that the β phase in the two-phase structure had a disordered BBC crystal since no superlattice reflections were observed at the [100] zone axis, as shown in Figure 4.26b. The rod-shape disordered β grains were observed to be separated from the retained B2 grains by an interface.
Figure 4.23. Optical micrographs showing the microstructure observed in the 1200°C-2min-WQ sample of alloy 4. (a) bright field micrograph; (b) dark field micrograph.
Figure 4.24. TEM micrographs showing the microstructure observed in the 1200°C-2min-WQ sample of alloy 4. (a) the thin foil specimen was tilted to the [001]_β zone axis of the β particles; (b) the thin foil specimen was tilted to the [001]_σ zone axis of the σ matrix.
Figure 4.25. Optical micrograph showing the microstructure observed in the 1000°C-2min-WQ sample of alloy 4.
Figure 4.26. Shows the microstructure observed in the 1000°C-2min-WQ sample of alloy 4. (a) TEM micrograph showing the reaction front of a colony that partially transformed from the B2 matrix; (b) SAED pattern showing the [100]_β zone axis of the disordered β phase located between the σ grains in the colony.
The transverse view of the colony structure near the interface between the colony and the retained B2 matrix is shown in Figure 4.27. The analysis at this orientation showed that this structure consisted of a continuous $\sigma$ matrix. The following orientation relationship between the $\sigma$ and the B2 phases was observed at this direction:

$$<001>_{B2} \parallel <001>_{\sigma} \text{ and } \{110\}_{B2} \parallel \{110\}_{\sigma}.$$ 

This orientation relationship is shown in the SAED pattern of Figure 4.27b. The micrograph in Figure 4.27a shows faceting along the $\sigma$/B2 interface and a high density of stacking faults predominantly along (100) and (010) planes in the $\sigma$ grain.

By correlating the diffraction pattern with the micrograph, it is observed that the (110)$_{\sigma}$ planes of the facets are parallel to the (110)$_{B2}$ planes of the retained B2 phase. It was also observed that the high number density of stacking faults caused the streaking that was observed in the diffraction pattern along the [100] and [010] directions of the $\sigma$ phase.

The transverse view near the center of the colony structure is shown in Figure 4.28. The micrograph in Figure 4.28a shows particles of the $\beta$ phase in a continuous $\sigma$ matrix. The convergent beam electron diffraction (CBED) pattern in Figure 4.28b shows that the $\beta$ particles have the disordered BCC structure and the following orientation relationship with the $\sigma$ phase at this direction:

$$<001>_{\beta} \parallel <001>_{\sigma} \text{ and } \{110\}_{\beta} \parallel \{110\}_{\sigma}.$$ 

This orientation relationship is shown in the SAED pattern of Figure 4.28b. The disordered structure of the $\beta$ phase was determined from the lack of superlattice reflections in the [001]$_{\sigma}$ zone axis.
Figure 4.27. Shows the microstructure observed in the 1000°C-2min-WQ sample of alloy 4. (a) TEM micrograph showing the transverse view of the colony structure near the interface between the colony and the B2 phase; (b) SAED pattern showing the orientation relationship between the B2 and $\sigma$ phases, which was $<100>_{\text{B2}} \parallel [001]_{\sigma}$ and $\{110\}_{\text{B2}} \parallel \{110\}_{\sigma}$. 
Figure 4.28. Shows the microstructure observed in the 1000°C-2min-WQ sample of alloy 4. (a) TEM micrograph showing the transverse view of the colony near the center of the colony; (b) CBED pattern showing the orientation relationship between the $\sigma$ and $\beta$ phases, which was $<100>_\beta \parallel [100]_\sigma$ and $\{110\}_\beta \parallel \{110\}_\sigma$. 

(a) 

500Å 

(b)
The analysis revealed that there were other possible orientation relationships between the \( \sigma \) and primary \( \beta \) phases. These additional orientation relationships were observed for the \( \sigma \) phase that precipitated from the primary \( \beta \) phase at temperatures above \( \sim 1200^\circ \text{C} \) and for the \( \sigma \) phase that formed in colonies from the primary \( \beta \) phase at \( 1000^\circ \text{C} \). It was determined that these orientation relationships involved the \([001]_\sigma\) zone axis, which was the 4-fold symmetry axis in the tetragonal structure of the \( \sigma \) phase. Figure 4.29 shows two of the additional orientation relationships that were commonly observed. The first orientation relationship is shown in Figure 4.29a:

\[
<1\bar{1}0>_\beta \| <1\bar{1}0>_\sigma \quad \text{and} \quad \{110\}_\beta \| \{110\}_\sigma.
\]

This orientation relationship is consistent with the previously shown one that was determined to be \(<001>_\beta \| <001>_\sigma \) and \(\{110\}_\beta \| \{110\}_\sigma\) since both of these orientation relationships are perpendicular to each other. The second orientation relationship is shown in Figure 4.29b:

\[
<1\bar{3}3>_\beta \| <001>_\sigma \quad \text{and} \quad \{110\}_\beta \| \{110\}_\sigma.
\]

The correlation that was made from these orientation relationships was that the \(\{110\}_\beta\) planes of the \( \beta \) phase were always parallel to the \(\{110\}_\sigma\) planes of the \( \sigma \) phase.

4.3 Discussion

In summary, the results of this study showed that alloys 2 and 4 solidified as the single \( \beta \)-phase with a disordered BCC structure. Upon cooling, the \( \beta \)-phase in both alloys underwent an order to disorder transition before the transformations of equilibrium phases occurred. The phase transformations were complicated in alloy 2 by the transformation of the metastable \( \omega \) phase and plates, in addition to the equilibrium phases. The formation of the metastable phases was observed to depend on the cooling rate from the aging temperatures.
Figure 4.29. SAED patterns showing two additional orientation relationships that were observed between the $\sigma$ and $\beta$ phases in the heat treated samples of alloy 4. (a) <110>$_{\beta_2}$ \parallel <110>$_{\sigma}$ and {110}$_{\beta_2}$ \parallel {110}$_{\sigma}$; (b) <113>$_{\beta_2}$ \parallel [001]$_{\sigma}$ and {110}$_{\beta_2}$ \parallel {110}$_{\sigma}$. 
In this chapter the discussion will focus on the equilibrium phases and their transformation mechanisms. The detailed analysis of the metastable phases observed in alloy 2 will be covered in chapters 5 and 6.

This discussion is divided into three sections: (1) the \( \beta \)-phase, (2) phase equilibrium, and (3) phase transformation mechanisms.

4.3.1 The \( \beta \) Phase

The results showed that the BCC \( \beta \) phase solidified as the primary phase in alloys 2, 3, and 4. This is in general agreement with recent data concerning the liquidus projection of the \( \beta \) phase in the Nb-Ti-Al ternary system [12].

The heat treatments proved that the \( \beta \) phase existed at elevated temperatures as a single phase from the \( \beta \)-solidus temperature to approximately 1400°C in alloy 2 and to between 1550°C and 1515°C in alloy 4. Therefore, these results combined with the as-cast results demonstrate the broad range in temperature and composition that the \( \beta \) phase has at elevated temperatures in the Nb-Ti-Al system and add to the results of previous studies [12,21,22,24,37]. The implication of these results is that basic physical metallurgy principles involving heat treatments and quenching procedures can be used for microstructural development [82,83].

It was shown in the as-cast and aged samples that the \( \beta \) phase exhibited a disorder to order transition in alloys 2 and 4. This was assessed by the presence of APDBs which formed during solid-state cooling from the high temperature disordered \( \beta \) structure to the low temperature ordered B2 structure.

A number of studies have shown that the B2 phase exists over an extensive composition range in the Nb-Ti-Al system [12,22,24,37]. The results of this study seem to support these findings since they showed the \( \beta \) phase to be ordered in alloys...
2 and 4. The fact that ordering was not observed in alloy 3 indicates that it depends on composition. The most significant difference between the composition of alloy 3 (10%Al) and alloys 2 (40%Al) and 4 (30%Al) was in the Al content of them. Therefore, it will be argued that Al is responsible for ordering in the β phase. These results differ from that generally accepted in the literature which correlate ordering with the Ti content [50].

A number of studies have shown a general trend indicating that Al always occupies a separate sublattice in various phases in the Nb-Ti-Al system, while Nb and Ti are found to occupy a sublattice either completely or at least limitedly. For instance, Konitzer et al. [47] determined that the 6h (Wyckoff designation) sites in α2-Ti3Al were occupied by Ti and Nb with neither substituting for Al on the 2d sites. In this same study by Konitzer et al., it was shown that Nb randomly substituted with Ti on 1a and 1c sites while Al occupied the 2e sites in a dilute Nb containing γ-TiAl phase. The same conclusion was obtained for the γ phase that was present in alloy 2 aged at 1200°C. Interestingly, the γ phase in alloy 2 contained up to ~22at.%Nb and yet the diffraction results were consistent with a random occupancy of Ti and Nb on the 1a and 1c sites (see section 4.2.2.1). Even in the stoichiometric Ti2AlNb orthorhombic phase examined by Mozer et al. [28] in which Ti occupied the 8g sites, Al occupied the 4c1 sites, and Nb the 4c2 sites [13], it was determined that Ti and Nb showed some degree of co-occupancy on the 8g and 4c2 sites but that neither substituted for Al on the 4c1 sites. The results of their study also showed that up to 18% of the 8g sites were occupied by Nb with the same fraction of 4c2 sites occupied by Ti. Finally, the study by Kohmoto et al. [49] showed that Al was responsible for
the \( \beta \) to B2 ordering, since the metastable B2 phase was observed in two binary Nb-Al alloys that contained only 13.5at.%Al and 16.9at.%Al.

This same site occupancy trend may also exist for the B2 phase. Even though the results by Banerjee et al. [50] showed that the 1a sublattice of the B2 phase was occupied preferentially by Ti and the 1b sublattice by both Nb and Al, this study still indicated that Al prefers to occupy sites on a separate sublattice. The co-occupancy between Al and Nb on one sublattice may simply be due to an insufficient amount of Al, since the alloy Banerjee et al. examined and even those examined by Kaufman et al. [25] had \( \approx 25 \) at.%Al. Therefore, only 50% of the sites on the sublattice could be filled by Al, while the rest had to be occupied by either Nb and/or Ti. It is also significant to note that Banerjee et al. determined that Nb and Ti (admittedly in limited quantities) co-occupied sites on both sublattices but that Al only occupied sites on one sublattice. This reasoning is consistent with the observations of alloy 3, in which ordering did not occur since it contained only \( \sim 10 \) at.%Al. This represented only a 20% site occupancy of the sublattice and was too small of a fraction for ordering to occur.

There still may be a preference between Ti and Al in the ordering behavior of the \( \beta \) phase. This may be understood better by considering the bonding between Nb, Ti, and Al. Nearest neighbor (NN) Lennard-Jones potentials [84] indicate that the Ti-Al bond is the most stable at \( \sim -56 \) kJ/mol with the Nb-Al bond just slightly less stable at \( \sim -51 \) kJ/mol. These values are significantly different from that of the Ti-Nb bond which was determined to be \( \sim -5 \) kJ/mol by BCC interaction parameter [69]. The latter agrees with the binary Ti-Nb phase diagram which shows a broad solubility range between Nb and Ti and no B2 ordering [10,11,72,73]. The slightly stronger
Ti-Al bond is stabilized by positioning Ti on the 1a Wyckoff sites and Al on the 1b sites. These sites represent the NN bonds, in terms of bond lengths, and are the shortest in the BCC structure. This atomic arrangement is shown in Figure 4.30 for (110) lattice planes of two unit cells of the ordered β (B2) phase. The NN bond is represented by the a/2<111> vector in this figure. The slightly less stable bond between Nb-Al results in a correspondingly slightly longer bond length. Therefore, it seems reasonable that Nb will preferentially occupy the 1b sites along with Al since the next-nearest-neighbor (NNN) bond in the BCC structure defines the lattice translation between two 1b sites, which is the a<001> vector shown in Figure 4.30. Thus, the slight difference between the Ti-Al and Nb-Al bond strength could account for the site occupancy results of Banerjee et al. [50] while still maintaining that Al is responsible for ordering in the β phase.

In summary, the general picture that develops from these considerations is that ordering in the β phase is due to Al adopting one of two sublattices. The other sublattice is preferentially filled by Ti due to the stronger bond between Ti-Al. Deficient sites on the Al sublattice are preferentially filled by Nb since its bond strength with Al is slightly weaker. However, in reality, an alloy with a ternary composition will deviate from these general rules and ultimately the ordering will be dictated by thermodynamic parameters.

There were also several anomalies that were consistently observed in the ordered β phase, regardless of whether it existed as the matrix or as retained particles in the microstructure. These anomalies were observed in the SAED patterns as the diffuse electron scattering, streaking, and spot splitting (Figures 4.2, 4.4, and 4.5). The matrix was also found to have a tweed microstructure which
Figure 4.30. Shows the translational vector for the nearest neighbor (NN) and next nearest neighbor (NNN) sites in the unit cell of the B2 phase. The atomic site occupancy shows Nb and Ti atoms randomly occupying the 1a Wyckoff site and Al atoms occupying the 1b Wyckoff site.
consisted of striations that were parallel to the \{1\bar{1}0\}_p planes in the <110>_p directions. The analysis of the tweed striations showed them to be visible or invisible depending on the \(g\) reflection. This indicated that strain was associated with the striations. This type of image characteristic was similar to that of dislocations, which can be made visible or invisible depending on the \(g\cdot b\) condition, where \(b\) is the Burgers vector of the dislocation and \(g\) is the reflection vector [85]. Thus, these observations were consistent with those from previous studies and indicated that the anomalies were caused by incommensurate shear strains on every other \{1\bar{1}0\}_p plane in the \(<1\bar{1}0>_p\) direction of the B2 phase [51-56]. The origin of the shear strains was attributed to phonons, which had the wave vector \(k = \frac{1}{2}<1\bar{1}0>\) and the polarization vector \(<110>\) [36,51]. The atomic displacements that result from these lattice shears was shown to be consistent with the heterogeneous deformation that occurs in the martensitic transformation of the 2H ortho-hexagonal phase from the \(\beta\) phase [36]. The results of this study seem to support this possibility for alloy 2, since a martensitic transformation of plates formed from the B2 phase was observed in this alloy during water quenching and during rapid solidification. This martensitic transformation will be covered in chapter 6.

4.3.2 Phase Equilibrium

The phase equilibria that was determined for alloys 2 and 4 is summarized using the flow diagrams shown in Figure 4.31. The results showed that the single disordered \(\beta\) phase was stable from the \(\beta\) solidus temperature down to the \(\sigma\) transus temperature in both alloys. The \(\sigma\) phase nucleated from the \(\beta\) phase at the \(\sigma\) transus temperature, which was slightly below 1400°C for alloy 2 and between 1550°C and 1515°C for alloy 4. These alloys had equilibrium two-phase \(\sigma + \beta\) microstructures.
below the σ transus temperatures. The σ and β phases were the equilibrium phases in the microstructures down to temperatures that were 1300°C in alloy 2 and below 1200°C in alloy 4. The phase equilibria that was observed below these temperatures was found to be different for alloys 2 and 4.

The microstructure in alloy 4 at 1000°C was determined to consist of the σ phase and O phase, which was based on the O-Ti2AlNb phase [13], in the long-term heat treated sample, but consisted of the σ and disordered β phases in the short-term heat treated sample. A possible reason for the different two-phase microstructures may have been due to an insufficient amount of time for the O phase to form during the short-term heat treated sample. This idea was based on previous studies that had shown the transformation of the O phase from the high temperature β/B2 phase to be time and temperature dependent [13,24-35]. These studies have shown that this transformation occurs either during slow cooling from the β/B2 phase, or during isothermal heating of the quenched and retained β/B2 phase. The composition of the retained β particles, which were present in the two-phase σ + β microstructures of alloy 4, was determined previously by Gomez [86]. In this study, the composition of the β particles was found to be ≈36Nb-43Ti-21Al (at.%), which indicated that the Ti and Al content were increased, while the Nb content was decreased compared to the composition of alloy 4 which was 42Nb-28Ti-30Al (at.%). Thus, the change in the composition of the β particles would have favored the formation of the O phase, provided that sufficient time was allowed for this phase to form. This suggests that the disordered β phase, which formed in 2 minutes during the short-term heat treatment, was a non-equilibrium phase that would have transformed to the O phase with a longer aging time.
Figure 4.31. Shows the equilibrium phases that formed at the aging temperatures in alloys 2 and 4. (a) alloy 2; (b) alloy 4.
Another consideration for explaining the formation of different two-phase microstructures in the 1000°C aging experiments of alloy 4 was the use of different cooling rates in the short-term and long-term aging experiments. In these experiments, the sample used in the short-term aging experiment was water quenched, while that in the long-term aging experiment was air cooled. It was thought that if the disordered β phase was in equilibrium at 1000°C, then the slow cooling rate used in the long-term aging experiments would have allowed the O phase to form at lower temperatures. However, the results by Kaufman et al. [25] showed that the O phase was stable in a 45Ti-25Al-30Nb (at.%) alloy at 1000°C. The composition of this alloy was close to the composition of the retained β particles in alloy 4 [86]. Therefore, the cooling rate effect was disregarded as a plausible explanation, since the long-term heat treatment of alloy 4 showed the presence of the O phase at 1000°C. Thus, it was concluded that the equilibrium phases of alloy 4 were the σ and O phases at 1000°C.

The different two-phase microstructures observed in alloy 2 at 1300°C and 1200°C indicated that a bivariant three-phase σ + γ + β tie-triangle crossed over the composition of 27Nb-33Ti-40Al (at.%) of alloy 2. It was determined that between these two temperatures, the σ + β microstructure which was present at 1300°C changed to the two-phase σ + γ microstructure which was present at 1200°C. The passage of the bivariant three-phase σ + β + γ field in alloy 2 is consistent with the reported liquidus projection of Perepezko et al. [12] and the 1200°C isotherm of Das et al. [22]. The liquidus projection, which was shown in Figure 2.3, showed that a class II four-phase reaction between L + σ + β and L + σ + γ occurred that produced the L + β + γ and β + σ + γ tie-triangles. The former tie-triangle continues along the
liquidus projection, while the latter persists to lower temperatures and was shown in the 1200°F isotherm in Figure 2.4. Because thermodynamics allows for two degrees of freedom in ternary three-phase equilibria, the compositions of the three-phases in the \( \beta + \sigma + \gamma \) tie-triangle can change as a function of temperature (with pressure fixed). Therefore, it can be asserted that at 1300°F the composition of alloy 2 was within the two-phase \( \sigma + \beta \) field that bordered on one side of the \( \sigma + \beta + \gamma \) tie-triangle. As the temperature decreased, the position of the tie-triangle shifted until it started to cross the composition of this alloy. At this point, the \( \beta \) phase started to disappear at the expense of the developing \( \sigma + \gamma \) phases. Upon passage of the tie-triangle, the composition of the alloy would then be within the two-phase \( \sigma + \gamma \) field.

4.3.3 Phase Transformation Mechanisms

4.3.3.1 Alloy 4

At high aging temperatures, the transformation of the \( \sigma \) phase from the \( \beta \) matrix occurs by nucleation and growth processes consisting of bulk diffusion. The ordered \( \beta \) phase retained upon quenching at room temperature becomes disordered upon heating to aging temperatures >1200°F. This was assessed from Figures 4.15 and 4.16 showing APDBs in the B2 grains that were formed during quenching from the aging temperatures. Therefore, these elements possessed high diffusivity rates at high aging temperatures, since the \( \beta \) phase has a disordered structure. This enabled long-range diffusion to occur through the \( \beta \) matrix, which would account for the nucleation of individual \( \sigma \) grains along the \( \beta \) grain boundaries and within the \( \beta \) matrix, as seen in Figures 4.14a-e.

The fully developed microstructures at the aging temperatures may consist of isolated \( \sigma \) grains in the \( \beta \) matrix, or of several \( \sigma \) grains that have grown and impinged
on one another, depending on the aging temperature. The \( \sigma \) grains are typically isolated from one another at temperatures greater than 1400\(^\circ\)C. As the aging temperature is decreased, the volume fraction of the \( \sigma \) phase increases relative to the \( \beta \) phase. At some point, the volume fraction increases to an extent that the \( \sigma \) grains start to impinge on one another. This process results in the change of the matrix from the \( \beta \) phase to the \( \sigma \) phase between 1400\(^\circ\)C and 1300\(^\circ\)C. This occurrence can be seen in Figure 4.14, which shows the \( \beta \) matrix at 1400\(^\circ\)C (Figure 4.14d) and the \( \sigma \) matrix at 1300\(^\circ\)C (Figure 4.14e). The impingement of the \( \sigma \) grains to form the matrix caused the particles of the retained \( \beta \) phase to become isolated in the microstructures that developed below the 1300\(^\circ\)C aging temperatures.

The different morphologies of the retained \( \beta \) particles were controlled by the formation mechanism of the \( \sigma \) grains. The irregular shaped \( \beta \) particles formed at the higher aging temperatures. At these temperatures, the long-range bulk diffusion processes caused the nucleation of isolated \( \sigma \) grains, which then grew with a convex curvature at the \( \sigma/\beta \) interface. The impingement of these \( \sigma \) grains led to the irregular shape of the retained \( \beta \) particles. At lowering aging temperatures, the \( \sigma \) grains were observed to form as a colony, with the retained \( \beta \) particles contained as inclusions. The colony structure was shown in Figure 4.21 for a number of closely oriented \( \sigma \) grains showing common [001] zone axes. However, the \( \sigma \) grains of a colony must have nucleated separately, since some of the [001] zone axes in the colony were rotated by as much as 45\(^\circ\) from one another. This would imply that high angle grain boundaries existed between the \( \sigma \) grains of the colony.

At the lower aging temperatures, the transformation resembles that of a discontinuous precipitation process \([87,88]\). Discontinuous transformations involve a
supersaturated matrix phase that reacts to form a lamellae made up of the depleted solid solution phase and the precipitated phase. The transformation is based on diffusional processes that occur at the migrating boundary of the reaction front. The diffusional requirement of this type of transformation is that the diffusivity of the boundary between the phases of the lamellae must be lower than the diffusivity of the reaction front. In this case, the lamellar spacing and the driving force are high enough for the surface energy of the reaction front to allow its migration. This type of transformation seems to have occurred at the temperature of 1000°C, where the metastable β phase remains supersaturated and ordered at this aging temperature. The ordered structure would lower the solute diffusion and make it more likely for diffusion to occur along grain boundaries, rather than through the bulk lattice. The reaction starts at the matrix grain boundary by precipitation of the secondary phase, in this case the σ phase, which advances into the matrix by solute diffusion along the advancing reaction grain boundary front. The reaction in this particular case can be written:

$$\beta' \rightarrow \beta + \sigma$$

where the β' phase is the ordered (B2) matrix, the β phase has the disordered structure and is the depleted solid solution, and the σ phase is the precipitated phase. The β and β' phases form an interface that acts as the reaction front. Confirmation of this type of reaction front was obtained in the 2 minute heat treatment of alloy 4 in which the transformation was "frozen in" by water quenching. The diffraction analysis clearly showed there to be β grains in conjunction with the σ grains in the transforming two-phase structure. The analysis also confirmed that the colonies formed at the β grain boundaries and grew into the matrix. It is suggested that the
same type of transformation occurred in the aged 1200°C and 1300°C samples, since colonies were observed by optical microscopy and verified by TEM to consist of large σ grains that contained a multitude of β inclusions.

There were several interesting aspects of the discontinuous transformation that were observed in this study. For instance, the precipitated σ phase was the major constituent of the two-phase microstructure. Therefore, the relationship of the σ phase with the β matrix appeared to control the formation of the colony. This was confirmed by showing several orientation relationships between the σ grains of the colony and the β matrix and by showing facets at the σ/β interface. Faceting was observed along the sides and at the reaction front of the transforming colonies. The analysis of the different orientation relationships consistently showed the \{110\}_σ planes to be parallel to \{110\}_β planes. These planes were also commonly observed as faceted planes at the σ/β interface. However, other facets were also observed, such as the one between \{100\}_β and \{100\}_σ planes. The facets imply that they have low interfacial energies and, because of this, they influence the crystallographic directions that the transformation front will proceed with in the matrix. Together these results have shown that crystallography plays a role in the nature of the discontinuous transformation observed in this study.

4.3.3.2 Alloy 2

The formation of the σ phase from the β phase below \(\approx 1400°C\) in alloy 2 occurs by nucleation and growth that requires long-range diffusion through the β matrix. This type of transformation is consistent with the formation of large blocky-shaped σ grains along primary β grain boundaries and within the β matrix of the 1300°C aged sample as shown in Figure 4.10c. The development of the σ + γ microstructure at
1200°C resembles that of an eutectoid transformation. This type of transformation occurs by the β phase, which was the matrix in the RAM sample, transforming to the σ + γ phases at the aging temperature. The eutectoid transformation is also based on nucleation and growth that requires diffusional processes.

The different morphologies of the σ + γ phases that were observed in the microstructures of the short-term and long-term 1200°C aged samples indicates that the development of these microstructures are affected by the heat rate. The lath morphology, which was observed in Figure 4.12 in the long-term aged sample, was formed by slowly heating the RAM sample from room temperature to 1200°C. In this heat treatment, the nucleation and growth of the σ and γ phases from the β matrix occurs below 1200°C. Therefore, it is expected that the diffusion path through the β matrix will be smaller at temperatures lower than at 1200°C, rather than at 1200°C. The transformation of the β phase to the σ + γ phases at the lower temperatures is thought to have occurred as a colony of these two phases. The diffusion occurs near the transformation front and has a path length that is in the order of the grain size observed for the σ and γ phases in the lath structures. The small diffusion path in the β matrix also causes the nucleation of new grains of the σ and γ phases ahead of the advancing transformation front. The equiaxed grain morphology, which was observed in Figure 4.22 for the short-term aged sample, was formed by rapidly heating the RAM sample to 1200°C. The nucleation of the σ and γ phases from the β phase occurs by site saturation, since the sample quickly reaches the aging temperature of 1200°C. The high number density of nuclei and the rapid diffusion rate at this temperature results in the formation of small equiaxed γ grains dispersed in the σ matrix.
The analysis of the short term aged samples revealed that the retained β phase transformed to the equilibrium microstructures very quickly at 1200°C and higher. This was demonstrated by aging a RAM sample for just two minutes at 1200°C and observing the equilibrium σ + γ phases in the microstructure, as shown in Figure 4.22. This result also indicates that the ω-related precipitates and plates that formed initially in the β matrix of the RAM sample dissolved rapidly to form the equilibrium σ + γ phases in this short amount of time. However, this transformation rate pertains to only phase equilibria and does not indicate how stable the microstructure is to grain coarsening processes.

It is unlikely that the initially complex microstructures observed in the as-cast samples had any affect on the development of the σ + β microstructure at 1300°C. This is based on the results which will be covered in chapter 5 and 6 that show the ω-phase and the plates are metastable phases that formed from the β phase without the need for long range diffusion. Therefore, the dissolution of these metastable phases should occur very fast at the high aging temperatures and that the ordered B2 phase should rapidly revert back to the disordered β phase.
CHAPTER 5
THE OMEGA-RELATED (ω-D) PHASE

5.1 Introduction

In chapter 4 on phase equilibria, it was shown that an ω-type phase had precipitated in the β matrix of the as-cast RAM sample of alloy 2. However, these precipitates were not observed in the heat treated and water quenched samples of alloy 2, or were they observed in alloy 4 which included the as-cast RAM and heat treated samples.

It was also previously shown that the ω-type precipitates that formed in alloy 2 had two size distributions which depended on their location in the microstructure. A high number density of small precipitates with a size range of ~0.05 µm were distributed homogeneously in the matrix as was shown in Figure 4.3b. There was no apparent interaction between them and the anti-phase domain boundaries that formed in the β matrix during the disorder to order transition. The large ω-type precipitates were usually connected to the lenticular precipitates (plates) as was shown in Figure 4.8b. The size range of these ω-type precipitates was between 0.5 and 1.0 µm.

The purpose of this chapter is to examine the transformation mechanism of the metastable ω-type phase from the β phase in greater detail. Results concerning the structure, the orientation relationship with respect to the β phase, and the temperature dependent parameters that affect the formation of this phase will be presented. This will be followed by a discussion of the transformation mechanism of
the \( \omega \) phase and will be treated in terms of a group/subgroup representation. It will be shown that the \( \omega \)-phase that was observed in alloy 2 is a new phase that was discovered in this study. Therefore, the discussion will also focus on its relation to the "family" of \( \omega \)-phases and will include a proposed site occupancy for it based on results obtained in this study.

5.2 Results

The results presented in this chapter cover the structural analysis of the \( \omega \)-type phase and the effect of heat treatment and cooling rate on its formation. The structural analysis section describes the determination of the crystal structure, the point group, the space group, the lattice parameters, and the orientation relationship with the \( \beta \)-phase and the plates. The other two sections deal with the influence of cooling rate and low heat treatment temperatures on the formation of the \( \omega \)-type phase.

5.2.1 Structural Analysis

5.2.1.1 Crystal Point Group and Space Group Determination

The crystal structure of the \( \omega \)-type phase was determined using CBED techniques on the large precipitates that formed in the as-cast RAM sample as was shown in Figure 4.8b of chapter 4. Figure 5.1 shows CBED patterns that were obtained from one of these precipitates. The CBED whole patterns observed in Figures 5.1a and 5.1b were obtained with a large and a small camera constant, respectively, and show 6-fold symmetry with two orthogonal mirror lines. It was found that the higher order laue zone (HOLZ) lines in the direct transmitted, or bright field, disc were never observed and that very faint first order laue zone (FOLZ) rings were occasionally observed, but only after very long exposure times. However,
Figure 5.1. CBED whole patterns showing the 6mm symmetry observed in the [0001] zone axis of the ω-related phase in alloy 2. (a) long camera length showing the zero order laue pattern; (b) short camera length showing the faint FOLZ rings.
when the FOLZ rings were observed, they always showed the 6mm symmetry in the CBED whole pattern. This result indicates that the structure of the $\omega$-type phase belongs to the 6mm1$_R$ projection diffraction group [89,90] as shown in Table 5.1. From this table, the two possible diffraction groups that belong to the 6mm1$_R$ projection diffraction group and show 6mm whole pattern symmetry are either the 6mm or 6mm1$_R$. Both of these symmetries are consistent with the hexagonal close packed (HCP) Bravais lattice. Therefore, the diffraction patterns shown in Figure 5.1 are consistent with the [0001]$_a$ zone axis.

The point group of the $\omega$-type phase was determined by CBED using a second zone axis of high symmetry, or the [1\bar100]$_a$ zone axis in this study, and is shown in Figure 5.2. These CBED whole patterns show 2mm symmetry for this zone axis using a large (Figure 5.2a) and a small (Figure 5.2b) camera constant. This result is consistent with the 2mm1$_R$ projection diffraction group, which has two possible diffraction subgroups associated with it as shown in Table 5.2 [89,90]. According to this table the two possible diffraction groups are either 2mm or 2mm1$_R$.

Finally, by combining the results of the [0001]$_a$ and [1\bar100]$_a$ zone axes, the point group of the $\omega$-type phase was identified. A compiled list from Buxton et al. [91] of all the possible point groups for each of the four diffraction groups is shown in Table 5.3. The examination of the table shows that there is only one point group that occurs for the diffraction groups of both zone axes. This is determined to be the 6/mmm point group and since there are no other point groups that meet this criterion, then this is the point group of the $\omega$-type phase.

The space group of the $\omega$-type phase was determined by noting the presence of additional translational symmetry elements, i.e. a screw axis and/or a glide plane.
Table 5.1. Shows the relation between the possible diffraction groups and the symmetries observed in the Convergent Beam Electron Diffraction (CBED) patterns at the \([0001]\) zone axis. [89].

<table>
<thead>
<tr>
<th>Observed Symmetry in Whole Pattern</th>
<th>Projection Diffraction Group</th>
<th>Possible Diffraction Groups</th>
<th>Whole Pattern Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>6mm</td>
<td>6mm&lt;sub&gt;R&lt;/sub&gt;1&lt;sub&gt;R&lt;/sub&gt;</td>
<td>6m&lt;sub&gt;R&lt;/sub&gt;m&lt;sub&gt;R&lt;/sub&gt;</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6mm</td>
<td>6mm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6&lt;sub&gt;R&lt;/sub&gt;m&lt;sub&gt;R&lt;/sub&gt;</td>
<td>3m</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6mm1&lt;sub&gt;R&lt;/sub&gt;</td>
<td>6mm</td>
</tr>
</tbody>
</table>
Figure 5.2. CBED whole patterns showing the 2mm symmetry observed in the [1T00] zone axis of the α-related phase in alloy 2. (a) long camera length showing the zero order laue pattern; (b) short camera length showing the FOLZ rings.
Table 5.2. Shows the relation between the possible diffraction groups and the symmetries observed in the Convergent Beam Electron Diffraction (CBED) patterns at the [1100]_o zone axis. [89].

<table>
<thead>
<tr>
<th>Observed Symmetry in Whole Pattern</th>
<th>Projection Diffraction Group</th>
<th>Possible Diffraction Groups</th>
<th>Whole Pattern Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>2mm</td>
<td>2mm1_R</td>
<td>2m_R,m_R</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2mm</td>
<td>2mm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2_R mm_R</td>
<td>m</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2mm1_R</td>
<td>2mm</td>
</tr>
</tbody>
</table>
Table 5.3. Shows the crystal point groups that are consistent with the diffraction groups observed in the CBED whole patterns. [89].

<table>
<thead>
<tr>
<th>Zone Axis</th>
<th>Diffraction Groups</th>
<th>Crystal Point Groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>[0001]</td>
<td>6mm</td>
<td>6mm</td>
</tr>
<tr>
<td></td>
<td>6mm1_R</td>
<td>6/mmm</td>
</tr>
<tr>
<td>[1T00]</td>
<td>2mm</td>
<td>mm2, 6m2</td>
</tr>
<tr>
<td></td>
<td>2mm1_R</td>
<td>mmm, 4/mmm, 6/mmm, m3, m3m</td>
</tr>
</tbody>
</table>
Figure 5.3 shows a CBED pattern of the [1100] zone axis that was observed to show evidence of both a screw axis and a glide plane. This pattern was obtained by tilting the specimen in order to position the kinematically forbidden (0001) reflection at the Bragg condition. This condition shows dynamic absences as a black cross, known as Gjonnes-Moodie lines or G-M lines, for the (0001) reflections [89] and indicates the simultaneous presence of both a screw axis and a glide plane in the structure. The presence of a screw axis at this zone axis is consistent with a $6_3$ screw axis that lies parallel to the (0001) plane normal. The glide plane determined from this orientation lies in the (0001) plane and is parallel to the [1120] direction, or is defined as a c-glide plane. To eliminate P6$_3$/mcc as a possible space group, the presence of a glide plane was checked at the [1120] zone axes but was not observed. These observations indicate that the space group of the $\omega$-type phase that was observed in alloy 2 is consistent with P6$_3$/mcm [43,92].

5.2.1.2 Orientation Relationship with the $\beta$ Phase

This investigation showed that the $\omega$-type precipitates had an orientation relationship with the $\beta$ matrix in the as-cast RAM sample. Figure 5.4 shows this orientation relationship:

\[ [0001]_\omega \parallel [111]_\beta \quad \text{and} \quad (1\overline{1}00)_\omega \parallel (1\overline{1}0)_\beta. \]

Reflections at $1/3(1\overline{1}0)_\beta$ positions correspond to $(1\overline{1}00)_\omega$ reflections and indicate that both lattice planes are parallel to each other.

The observed orientation relationship indicates that twelve variants were formed in the transformation. Four rotational variants were produced by aligning the [0001]$_\omega$ direction of each variant parallel to each of the four $<111>\beta$ directions. There were then three translational variants that were formed by aligning the $(1\overline{1}00)_\omega$
Figure 5.3. CBED whole pattern of the [1T00] zone axis with the beam tilted slightly to show the black cross in the kinematically forbidden (0001) reflection at the Bragg condition.
Figure 5.4. SAED pattern showing the orientation relationship that was observed for the ω-related and B2 phases. The OR was determined to be $[0001]_\omega \parallel [111]_p$ and $(\overline{1}000)_\omega \parallel (1\overline{1}0)_p$. 
planes parallel to each of the three \(\{1\overline{1}0\}\) planes of the four rotational variants. Therefore, the SAED pattern shown in Figure 5.4 can consist of diffraction spots from all twelve variants, which would be superimposed on the \([111]\) zone axis. The twelve variants would be accounted for in this diffraction pattern by the \([0001]_w\), \([\overline{4}223]_w\), \([2\overline{1}23]_w\), and \([22\overline{1}3]_w\) zone axes.

The orientation relationship between the \(\omega\)-type and \(\beta\) phases is also shown in the stereographic projection of Figure 5.5. The projection shows the \([0001]_w\) and \([111]\) poles and represents one of the four rotational variants. The intersection of the three \(<\overline{4}223>_w\) poles with the three other \(<\overline{1}11>_w\) poles is seen in this projection. This accounts for the possibility of three additional rotation variants that can be superimposed on the \([0001]_w\) variant at the \([111]\) zone axis.

Figure 5.6 shows the SAED pattern of the \(\omega\)-type phase at the \([110]\) zone axis. It consists of two zone axes obtained from two grains of the \(\omega\)-type phase, the \([1\overline{1}00]_w\) and \([10\overline{1}0]_w\) that are superimposed on the \([110]\) zone axis. The pattern shows that the \([0001]_w\) reflections from both grains are parallel to the \((\overline{1}11)_p\) and \((1\overline{1}1)_p\) reflections and that the diffraction intensity is greater for one of the grains. The very faint diffraction spots observed at \(1/3\{1\overline{1}0\}_p\) positions correspond to the \([1\overline{1}00]_w\) reflections of \(\omega\)-type precipitates oriented at the \(<11\overline{6}>_w\) zone axes. These originate from the small \(\omega\)-type precipitates that were within the selected area diffraction aperture when the pattern was recorded.

5.2.1.3 Orientation Relationship with the \(\beta\) Phase and Plates

In addition to forming an orientation relationship with the \(\beta\) phase, the \(\omega\)-type precipitates also formed one with the plates that were present in the as-cast microstructure. Figure 5.7 shows an area of the microstructure containing all three
phases and the SAED pattern of the orientation relationship. The analysis of the
diffraction pattern with the plates indexed according to the (O) orthorhombic
structure showed the following orientation relationship:

\[
[0001]_\omega \parallel [110]_\omega \parallel [111]_\beta \quad \text{and} \quad (\bar{T}100)_\omega \parallel (001)_\omega \parallel (110)_p.
\]

The relationship observed between the \(\omega\) and \(\beta\) phases is the same as previously
shown in Figure 5.4. The relationship observed between the plates and the \(\beta\) phase
will be discussed further in chapter 6. The micrograph in Figure 5.7a shows three
rotational variants of the plates. These are marked 1, 2, and 3 and are rotated 60°
relative to each other. The large \(\omega\) grain is marked with the \(\omega\) symbol and is observed
to be connected to the plates. An interesting observation made in the micrograph
was the V-shape of the \(\omega\) grain in contact with the two plates. This observation will
be considered later in the discussion since it may provide information concerning the
order in which the \(\omega\) phase and the plates formed from the \(\beta\) phase.

The diffraction pattern in Figure 5.7b is composed of several patterns that are
all superimposed on the [111]_\(\beta\) zone axis. The detailed analysis of this composite
pattern is shown in the calculated diffraction patterns of Figure 5.8. Figure 5.8a
shows the composite of five diffraction patterns from the \(\beta\) matrix, \(\omega\) precipitate, and
three plates. Figures 5.8b to 5.8f show the individual patterns of these phases. The
[111]_\(\beta\) zone axis of the \(\beta\) matrix is shown in Figure 5.8b. The [0001]_\(\omega\) zone axis of the
\(\omega\)-type phase is shown in Figure 5.8c and corresponds to the grain marked with the \(\omega\)
symbol in the micrograph (Figure 5.7a). The next three diffraction patterns shown in
Figures 5.8d to 5.8f are from the three plates marked 1, 2, and 3 in the micrograph.
The three diffraction patterns show the same [110]_\(\omega\) zone axis of the plates and are
rotated relative to each other by 60°. This rotation results from the orientation
Figure 5.5. Shows the stereographic projection of the OR relationship that was observed for the \( \alpha \)-related and \( \beta \) phases in alloy 2. The projection shows the [111]_\( \beta \) and [0001]_\( \alpha \) poles.
Figure 5.6. SAED pattern showing the OR between the α-related and β phases at the [110]_β zone axis. Two rotational variants with the [1T00]_α and [10T0]_α zone axes are superimposed on this diffraction pattern.
Figure 5.7. Shows the microstructure observed in the as-cast sample of alloy 2. (a) TEM micrograph showing three plates and a coarse ω-related grain observed in the B2 matrix; (b) SAED pattern showing the orientation relationship observed for the three plates, the ω-related grain, and the B2 phase at the [111]_p zone axis.
Figure 5.8. Shows the calculated diffraction patterns of the three plates and the coarse ω-related grain at the [111] zone axis of the B2 matrix. (a) the composite pattern; (b) the [111] zone axis of the B2 matrix; (c) the [0001] zone axis of the ω-related grain; (d) the [110] zone axis of the orthorhombic plate 1; (e) the [110] zone axis of the orthorhombic plate 2; (f) the [110] zone axis of the orthorhombic plate 3.
relationship that the plates have with the β phase (discussed further in chapter 6) which causes the (001) planes of the plates to lie parallel to each of the three \{1\overline10\}_β planes of the β phase.

5.2.1.4. Lattice Parameter Determination

The lattice parameters of the ω phase were determined from SAED patterns. The a-axis parameter was calculated from the d-spacing measurements of the \{1\overline100\} reflections at the [0001]_ω zone axis. The c-axis parameter was determined directly from the d-spacing measurements of the (0001) reflection at both the [1\overline100]_ω and [11\overline20]_ω zone axes. These measurements indicated that the lattice parameters of the a-axis was 7.96Å and the c-axis was 5.63Å.

It was determined from the diffraction analysis that the lattice parameters of the ω phase were related to the lattice parameter of the β phase in the following manner: \(a_ω = \sqrt{6}a_β\) and \(c_ω = \sqrt{3}c_β\). These relationships corresponded to the d-spacings between the \{1\overline100\}_ω and \{112\}_β planes for \(a_ω\) and between the (0001)_ω and the \{111\}_β planes for \(c_ω\).

5.2.2 Effect of Cooling Rate

The investigation of the effect of cooling rate on the formation of the ω-type phase involved heating a RAM sample of alloy 2 to 1400°C for 4 hours and furnace cooling it in the vacuum furnace. The microstructure that developed in this sample was compared to that of the water quenched sample under the same heat treatment conditions (see Figures 4.10 and 4.11).

An optical micrograph showing the microstructure observed in the furnace cooled sample is shown in Figure 5.9. It consisted of straight grain boundaries with triple points and a homogeneous distribution of acicular shaped precipitates in the
matrix region. However, the acicular precipitates were not observed along some regions of the grain boundaries. The microstructure in these regions resembled that of a discontinuous type transformation that was in progress. These observations are consistent with the results obtained in the phase equilibria study (chapter 4) which indicated that only the β phase existed at the aging temperature of 1400°C. The additional phases that are observed in the optical micrograph of Figure 5.9 occurred during solid state cooling.

The TEM analysis of the furnace cooled sample identified two regions in the microstructure that were comprised of different phases. Figure 5.10 shows the microstructures of these two regions. The microstructure of the in-matrix region (Figure 5.10a) was complex, but was determined to consist of just two phases. The matrix in this region consisted of an interconnected network of small grains, or domains, of the ω-type phase, which showed the same crystal structure as those of the as-cast RAM sample. The second phase in this region consisted of plates that were distributed in the matrix. These plates were the same as those identified in the heat treated and water quenched samples of this alloy. The grain boundary region (Figure 5.10b) was less complicated than the in-matrix region and also consisted of two phases. The matrix was composed of large σ grains with a number of small γ grains distributed at the σ grain boundaries. The microstructure of this region was similar in appearance to that of the equilibrium σ + γ microstructure that was observed in the 1200°C aged sample (compare to Figure 4.12).

The results of this investigation indicate that the ω-type phase is affected by the cooling rate from elevated temperatures and that a slow cooling rate results in the formation of the ω-type phase, instead of plates. However, if the cooling rate is
Figure 5.9. Optical micrograph showing the microstructure observed in the 1400°C-4hrs-FC sample of alloy 2.
Figure 5.10. TEM micrographs of the 1400°C-4hrs-FC sample of alloy 2. (a) the in-matrix region consisting of the ω-related phase and plates; (b) the prior grain boundary region consisting of the σ and γ phases.
very slow, then the \( \sigma \) and \( \gamma \) phases will form instead of either the \( \omega \)-type phase or plates.

5.2.3 Effect of Low Temperature Heat Treatments

The investigation of the effect of low temperature on the formation of the \( \omega \)-type phase was conducted with RAM samples that were heat treated at 400°C and at 600°C for 12 hours.

The TEM analysis of the sample aged at 400°C did not show any significant changes in the microstructure as compared to the as-cast condition. The APDBs that formed in the \( \beta \) matrix of the as-cast sample were still present after aging. However, it was determined that the \( \omega \)-type precipitates that formed in the \( \beta \) matrix were larger in size than in the as-cast microstructure. Both of these observations are shown in Figure 5.11. The increase in the size of the \( \omega \) precipitates can be observed by comparing Figure 5.11a of the 400°C aged sample with Figure 4.3 of the as-cast sample. There also appeared to be more \( \omega \) precipitates that were attached to the APDBs in the \( \beta \) matrix following the 400°C aging treatment. This is observed in Figure 5.11b, which can also be compared with Figure 4.3 of the as-cast sample.

The effect that temperature had on the microstructure of alloy 2 was more pronounced in the 600°C aged sample than in the 400°C aged sample. It was found that the entire B2 matrix, which was present in the as-cast microstructure, had completely transformed to the \( \omega \)-type phase in the 600°C aged sample as shown in Figure 5.12. However, the analysis showed that this aging temperature did not affect the grain boundary \( \gamma \) allotriomorphs and in-matrix plates that were present in the as-cast sample, since no further nucleation, growth, or dissolution of these phases was observed. The analysis of the transformed \( \omega \)-type phase showed that there were
Figure 5.11. TEM micrographs of the 400°C-12hrs-WQ sample of alloy 2. (a) shows the precipitates of the α-related phase observed in the B2 matrix; (b) shows the APDBs observed in the B2 matrix.
Figure 5.12. TEM micrographs of the 600°C-12hrs-WQ sample of alloy 2. (a) shows the fine \( \omega \)-related domains that formed from the B2 phase; (b) shows the coarse \( \omega \)-related domains that formed at the prior B2 grain boundaries.
two size distributions that depended on the location in the microstructure. The small domains were ≤200Å in size and were observed in the prior B2 matrix region (Figure 5.12a), while the coarse domains were ~0.1 to 0.5μm in size and were observed near the prior B2 grain boundaries and prior plates (Figure 5.12b). The coarse domains that were present in the 600°C aged sample were similar in size to those that were observed in the as-cast RAM sample (compare Figure 5.12b to Figure 4.8b).

The SAED patterns that are shown in Figure 5.13 were from four different zone axes of the prior B2 phase that transformed to the ω-type phase. The four zone axes were identified according to the B2 phase as the [111]₀ (Figure 5.13a), the [110]₀ (Figure 5.13b), the [100]₀ (Figure 5.13c), and the [112]₀ (Figure 5.13d). The [111]₀ and [110]₀ zone axes were similar to those previously shown in Figure 5.9 of the structural analysis. From the previous analysis of the [111]₀ and [110]₀ zone axes, the four SAED patterns shown in Figure 5.13 indicated that the microstructure shown in Figure 5.12 consisted of three translational variants for each of the four rotational variants, or twelve total variants, of the ω-type phase.

The analysis of the coarse ω-type domains in the 600°C aged sample revealed the presence of internal interfaces that resembled APDBs. The typical appearance of this type of interface is shown in Figure 5.14. This interface was observed in a single rotational variant of the ω-type phase at the [110]₀ zone axis using the $g=(1120)_ω$ reflection. These interfaces were wavy in shape and were never seen to intersect with other similar types of interfaces. This observation indicated that these were translational interfaces and was confirmed by the SAED analysis that showed no extra reflections that would have indicated two rotational variants.
Figure 5.13. SAED patterns from the 600°C-12hrs-WQ sample of alloy 2 that show the diffraction patterns of the former B2 matrix. (a) [111]_{B2} zone axis; (b) [110]_{B2} zone axis; (continued)
Figure 5.13. (continued) (c) \([100]_{B_2}\) zone axis; (d) \([112]_{B_2}\) zone axis.
Figure 5.14. TEM micrograph of the 600°C-12hrs-WQ sample of alloy 2 that shows the APDBs observed in a coarse rotational domain of the \(\omega\)-related phase. The \(g = (11\overline{2}0)\) reflection was used to show the APDBs in the coarse domain.
5.3 Discussion

In summary, the results of this investigation showed that an \( \omega \)-type phase (referred to as \( \omega \)-D from this point on) transformed from the high temperature \( \beta \) phase in alloy 2. It was determined from the as-cast RAM and the furnace cooled samples that a slow cooling rate favored the \( \omega \)-D transformation relative to that of the plates which formed during rapid cooling rates. The structural analysis of the \( \omega \)-D phase indicated that it was similar in many ways to the "family" of \( \omega \) phases, however, there were also several differences. The significance of these differences was that they indicated that the \( \omega \)-D phase was a new phase in the ternary Nb-Ti-Al system that was identified in this study.

The discussion that follows will cover many aspects of the B2 phase to \( \omega \)-D phase transformation that occurred in alloy 2. The observed orientation relationship, hexagonal structure, and diffuse scattering all signify that the \( \omega \)-D phase transformed from the B2 phase analogous to the \{111\}_p plane collapse mechanism [48]. However, there were several differences which separated the \( \omega \)-D phase from the previously reported \( \omega \) related phases. It will be shown that these differences are caused by the ordering in the \( \omega \)-D phase which changed the symmetry, lattice parameters, and modified the orientation relationship as compared to the \( \omega \)-related phases of this ternary system. The site occupancy of the \( \omega \)-D phase will then be shown to be consistent with the experimental observations. Finally, the crystallographic aspects of the \( \beta \) to \( \omega \)-D phase transformation will be discussed based on consistencies with the experimental observations and with previous work by Bendersky et al. [37].
5.3.1 Microstructural Aspects of the $\omega$-D Phase

The results of this study indicated that the composition of the $\omega$-D phase must be close to the composition of alloy 2, which is 27Nb-33Ti-40Al (at.%). The $\beta$ phase in the as-cast microstructure transformed completely to the $\omega$-D phase upon slow cooling from 1400°C and upon holding at 600°C. The small amount of $\gamma$ phase that was present in the as-cast microstructure before the heat treatments was not expected to have much effect on the composition of the $\beta$ phase matrix and neither was the plates since they will be shown in chapter 6 to form by a displacive transformation. Results similar to these were observed by Bendersky et al. [37] when they performed heat treatments at 700°C and higher followed by furnace cooling in an alloy with the Ti$_4$Al$_3$Nb composition. The significance of this observation is that when it is used with the results from the structural analysis then the site occupancy of the $\omega$-D phase may be determined.

The results of the microstructural characterization showed that the precipitation of the $\omega$-D phase occurred homogeneously and with limited diffusion from the ordered $\beta$ (B2) matrix. This was determined from Figure 4.3, which showed a very high number density of small $\omega$-D precipitates that nucleated within the B2 matrix of the as-cast sample. The fact that $\omega$-D precipitates did not nucleate on the APDBs of the B2 matrix is consistent with this assessment. It is expected that the APDBs should have acted as a heterogeneous nucleation source for the $\omega$-D precipitates since this was observed by Strycor et al. [36] in their investigation. The results obtained from the 400°C aged sample suggested that the $\omega$ precipitates can nucleate without long-range diffusion, since the APDBs in the B2 matrix were unaffected by this aging temperature as shown in Figure 5.11b. This observation
indicates that diffusion in the B2 matrix did not occur or this would have destroyed the $a/2\langle111\rangle_\beta$ APDB vector. The lack of long range diffusion is consistent with results that show a decrease in diffusion rates in ordered BCC phases after the disorder to order transition [93]. Therefore, if $\omega$ precipitates formed at 400°C as postulated, then they did so without the need for long-range diffusion. Thus, these observations indicated that the $\omega$-D phase nucleated from the ordered $\beta$ (B2) matrix of alloy 2 after the disorder to order reaction, that formed the APDBs, had occurred. These observations also suggest that the transformation occurred with limited diffusion in the B2 matrix.

The coarse $\omega$-D grains that were observed adjacent to the plates suggests a heterogeneous nucleation mechanism. It was shown in Figure 5.7 that an $\omega$-D grain had a V-shape morphology that resulted from the impingement of two plates. This observation may imply that the plates formed from the B2 phase before the formation of the $\omega$-D grains. If this scenario were to have occurred, then the coarse $\omega$-D grains could have then nucleated at the interface of the plates at a higher temperature than the fine in-matrix $\omega$-D precipitates. This could have occurred since heterogeneous nucleation events occur at higher temperatures, or lower undercoolings during quenching, than homogeneous nucleation events. The higher nucleation temperature would facilitate faster diffusion rates, which would cause more rapid grain growth. This appears to be consistent with the observations in this study since lower temperatures would result in limited diffusion and in the formation of smaller in-matrix $\omega$-D precipitates. However, an apparent contradiction to this was determined from the analysis of the plates, which showed that these plates formed from the B2 matrix by a displacive transformation that required no long-range
diffusion (see chapter 6). This result supports the notion that long-range diffusion is not required for the precipitation of both fine and coarse \( \omega \)-D grains. Thus, there is some uncertainty as to why the \( \omega \)-D grains that nucleated heterogeneously on the plates were larger than the in-matrix \( \omega \)-D precipitates.

There is a possibility that the large \( \omega \)-D grains have a different crystal structure than the small in-matrix \( \omega \)-D precipitates. This possibility arises from the results of Bendersky et al. [8] in which coarse and fine \( \omega \) grains were observed intermixed together in the transformed B2 matrix. Their analysis showed that the fine grains had trigonal P\( 3 \)\( m \)\( 1 \) (\( \omega'' \)) symmetry which resulted from the incomplete collapse of the double layers during the transformation. In comparison, the coarse \( \omega \) grains were found to have hexagonal P\( 6_3 \)\( \text{mmc} \) (\( \omega \)-B\( 8 \)) symmetry, which resulted from chemical ordering and complete collapse of the double layers. The results of this study also showed that the large \( \omega \)-D grains had hexagonal symmetry and P\( 6_3 \)/mcm space group. Unfortunately, this symmetry could not be verified using CBED analysis for the in-matrix \( \omega \) precipitates due to the small size. However, it was interesting that the SAED patterns of the small in-matrix \( \omega \) precipitates of the as-cast microstructure showed the presence of 1/3\{110\}_\( \beta \) reflections. Furthermore, these reflections were also observed in SAED patterns of the \( \omega \) precipitates present in the fully transformed microstructure of the 600\( ^\circ \)C heat treated sample. These reflections were determined to correspond to the \{1\( \overline{1} \)00\}_\( \omega \) lattice planes of the \( \omega \)-D phase based on the hexagonal structure. Thus, if the small in-matrix \( \omega \) precipitates have trigonal symmetry, then they must also share a similar chemical ordering to that of the hexagonal structure. The difference between the two structures may then be due only to the incomplete collapse of the double layer and partial ordering on the
single layers. This seems likely since the in-matrix \( \omega \) precipitates were previously
determined to have formed at low temperatures where atomic movement is limited.

5.3.2 Comparison of the \( \omega \)-Related Phases in the Nb-Ti-Al System

A comparison will be made in this section between the \( \omega \)-D phase discovered in
this investigation and the \( \omega \)-related phases from the literature. This comparison will
only include the \( \omega \)-Ti (disordered) [48] and the \( \omega \)-B\( \text{B}_2 \) [36, 37] phases that have
hexagonal crystal structures. The trigonal \( \omega \) structure will not be included since it is
considered an intermediate structure that results from the incomplete transformation
of the \( \beta \) phase to the hexagonal \( \omega \) phase [48, 37]. Table 5.4 shows the results of this
comparison.

The results indicate that the \( \omega \)-D phase has several characteristics that are
similar to those of the \( \omega \)-related phases. It possesses a hexagonal crystal structure
that has 6/mmm point group symmetry. It forms from the \( \beta \)-phase with the \((0001)_{\omega}\)
planes parallel to the \(\{111\}_p\) planes, or similarly, with the \((0001)_{\omega}\) plane normal
parallel to the \(\{111\}_p\) plane normal. Furthermore, in terms of the parent \( \beta \) phase,
diffuse electron scattering with intensity maxima's near \( 1/3\{111\}_p \) reflections are
present in the diffraction patterns. These scattering anomalies are commonly
observed in \( \omega \) forming systems and are associated with atomic displacements along
the \( <111>_p \) direction. These similarities suggest that the transformation mechanism
of the \( \omega \)-D phase is analogous to that which has been determined for the \( \omega \)-related
phases [48].

However, there were some differences that also existed between the \( \omega \)-D phase
and the \( \omega \)-related phases. These differences included changes in the space group, the
orientation relationship with the \( \beta \) phase, and the lattice parameters.
Table 5.4. Comparison of characteristics between the ω-D, the disordered ω-Ti, and the ordered ω-B8₂ phases from the Nb-Ti-Al ternary system.

<table>
<thead>
<tr>
<th>ω-phase</th>
<th>Point Group</th>
<th>Space Group</th>
<th>Lattice Parameters*</th>
<th>Orientation Relationships</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>a(Å)</td>
<td>aₜ/aₚ relation</td>
</tr>
<tr>
<td>ω-Ti</td>
<td>P/mmm</td>
<td>P/mmm</td>
<td>4.60</td>
<td>aₜ=√2aₚ</td>
</tr>
<tr>
<td>ω-B8₂</td>
<td>P/mmm</td>
<td>P6₃/mmc</td>
<td>4.60</td>
<td>aₜ=√2aₚ</td>
</tr>
<tr>
<td>ω-D</td>
<td>P/mmm</td>
<td>P6₃/mcm</td>
<td>8.03</td>
<td>aₜ=√6aₚ</td>
</tr>
</tbody>
</table>

* the values listed for the lattice parameters were obtained using the relations shown in the column to the right of them with aₚ = 3.28Å.
In terms of the space group, the \( \omega \)-D phase was determined by CBED analysis to have the P6\(_3\)/mcm space group symmetry. This differs from the P6/mmmm space group of the disordered \( \omega \)-Ti phase [48] and the P6\(_3\)/mmc space group of the \( \omega \)-B8\(_2\) phase [36,37]. Bendersky et al. [37] proved that the 6\(_s\) screw axis and the c-glide plane in \( \omega \)-B8\(_2\) resulted from chemical ordering. Since both of these translational symmetry elements were also observed in the \( \omega \)-D phase, then this indicates that chemical ordering also occurred in the structure. The chemical ordering has to be different, however, since the c-glide plane changed from the \{1\( \bar{T} \)0\}_\( \omega \) plane in the \( \omega \)-B8\(_2\) phase to the \{11\( \bar{2} \)0\}_\( \omega \) plane in the \( \omega \)-D phase. This represents a 90\(^\circ\) rotation around the [0001]\(_\omega \) screw axis and results in a symmetry change from the P6\(_3\)/mmc space group of the \( \omega \)-B8\(_2\) phase to the P6\(_3\)/mcm space group of the \( \omega \)-D phase.

It was also observed in the orientation relationships that the \{1\( \bar{T} \)00\}_\( \omega \) planes of the \( \omega \)-D phase were parallel to the \{1\( \bar{T} \)0\}_\( \beta \) planes at the [0001]\(_\omega \) \( \| \) [111]\(_\beta \) zone axes. For the \( \omega \)-Ti and \( \omega \)-B8\(_2\) phases, the \{11\( \bar{2} \)0\}_\( \omega \) planes lied parallel to the \{1\( \bar{T} \)0\}_\( \beta \) planes. This difference amounted to a 30\(^\circ\) rotation between the unit cells of the \( \omega \)-D phase and the \( \omega \)-Ti and \( \omega \)-B8\(_2\) phases with reference to the lattice of the \( \beta \) phase. This result was consistent with the 90\(^\circ\) rotation that was observed in the c-glide plane between the \( \omega \)-B82 and \( \omega \)-D phases.

Finally, the dimensions of the unit cell for the \( \omega \)-D phase were considerably larger than that of the \( \omega \)-related phases. The comparison shown in Table 5.4 shows that the \( a \)\(_\omega \) parameter for the \( \omega \)-D phase is 8.03Å which is larger than 4.60Å for both the \( \omega \)-Ti [48] and the \( \omega \)-B8\(_2\) phases [36,37]. These values were calculated from the lattice correspondence between the \( \beta \) and \( \omega \) phases as seen in the orientation relationships. As an example for the \( \omega \)-D phase, the <112>\(_\beta \) direction was observed to...
lie parallel to the $<11\bar{2}0>$ direction which then defines the $a_0$ lattice parameter of
the hexagonal unit cell. The unit length of the $<11\bar{2}>_\beta$ direction in the BCC unit cell
is equal to $\sqrt[3]{6}a_\beta$, which gives 8.03Å for $a_\beta = 3.28\text{Å}$. Therefore, the relationship
showing $a_0 = \sqrt[3]{6}a_\beta$ is then obtained for the $\omega$-D phase. In comparison, the orientation
relationship that has been observed for the $\omega$-Ti and $\omega$-B$_8$ phases indicates that the
$<110>_\beta$ direction lies parallel to the $<11\bar{2}0>_{\omega}$ direction. The unit length of the $<110>_\beta$
direction in the BCC unit cell is equal to $\sqrt{2}a_\beta$, which gives 4.60Å for $a_\beta = 3.25\text{Å}.$
Thus, the relationship showing $a_0 = \sqrt{2}a_\beta$ is then obtained for the $\omega$-Ti and $\omega$-B$_8$
phases.

A comparison of the $c_\omega$ lattice parameter of the $\omega$-D phase shows that it is the
same as that of the $\omega$-B$_8$ phase, however, it is twice that of the $\omega$-Ti phase. This
determination was based on the relationship between $c_\omega$ and $c_\beta$ lattice parameters
which showed it to be $c_\omega = \sqrt{3}a_\beta$ for the $\omega$-D and $\omega$-B$_8$ phases and $c_\omega = (\sqrt{3}a_\beta)/2$ for the
$\omega$-Ti phase. These relationships were derived in a similar manner as described before
except that they relate the [0001]$_\omega$ direction to the $<111>_{\beta}$ direction. The $\sqrt{3}$ and $\sqrt{3}/2$
terms are derived from the body diagonal of the BCC unit cell which has a length of
$\sqrt{3}a_\beta$, or 5.68Å assuming $a_\beta = 3.28\text{Å}$. This length is the same as the $c_\omega$ lattice
parameter of the $\omega$-D and $\omega$-B$_8$ phases, but it is twice that of the $\omega$-Ti phase which is
2.84Å or 1/2 the $<111>_{\beta}$ diagonal.

5.3.3 Transformation and Site Occupancies of the $\omega$ Phases

The transformation of the $\omega$ phase from the cubic $\beta$ phase has been studied
extensively in the past and was examined briefly in the literature review of chapter 2.
The purpose of this section will be to examine the $\omega$ phase transformations that have
been studied in the Nb-Ti-Al system. In particular, the relationship between the site
occupancies of the parent $\beta$ phase and the product $\omega$ phase will be examined. Finally, the site occupancy of the $\omega$-D phase will be proposed based on its relationship with the site occupancies of the B2 phase in alloy 2 and the $\omega$-B8$_2$ phase analyzed by Bendersky et al. [37].

5.3.3.1 The $\omega$-Ti and $\omega$-B8$_2$ Phases

The transformation of the $\beta$-Ti phase to the $\omega$-Ti phase involves disordered structures of both phases and is shown in the schematic of Figure 5.15. The BCC unit cell of $\beta$-Ti has two lattice sites at (0,0,0) and ($\frac{1}{2},\frac{1}{2},\frac{1}{2}$) at 2a Wyckoff positions and that are occupied by Ti atoms (or a random solid-solution). The atoms at these sites are shifted during the transformation such that atoms on every third \{111\}$_{\beta}$ plane (layers 0 and 3) remain undisturbed, but atoms on the other two successive planes (layers 1 and 2) are displaced towards each other. The latter process describes the collapse that forms the double layer in the $\omega$ structure. If the collapse is incomplete, i.e. the double layer is non planar or commonly referred to as rumpled, then the $\omega$ phase has $P\overline{3}m1$ trigonal symmetry [48]. However, if the collapse is complete, then the hexagonal $\omega$ structure with P6/mmm symmetry results and the double layer is planar. The structure in this case has three lattice sites at 1a (0,0,0) and 2d ($\frac{1}{3},\frac{2}{3},\frac{1}{2}$) Wyckoff positions and that are occupied by Ti atoms. The dimension of the hexagonal $\omega$-Ti unit cell along the c-axis is half the length of the body diagonal in the BCC $\beta$-Ti unit cell, or $a_\beta/2<111>_{\beta}$.

The same treatment applies to the transformation of the B2 phase to the $\omega$-B8$_2$ phase except that both phases in this case have ordered structures. This transformation was examined in detail by Bendersky et al. and related the site occupancies of the B2 phase to the $\omega$ phases [37]. A schematic of the site occupancies
Figure 5.15. Shows the atomic site occupancies of the disordered β phase and the disordered ω phase for Ti.
for these two phases from their study is shown in Figure 5.16. The site occupancy information that they used for the B2 phase was from previous work by Banerjee et al. [50] which showed that Ti atoms occupied the 1a Wyckoff position at (0,0,0) and Al plus Nb atoms co-occupied the other 1b Wyckoff position at (½,½,½). The BCC unit cell is shown in this schematic along the [111]_B body diagonal and, therefore, the 1b Wyckoff position is located at half of this length along this direction. The structure of the ω-B8₂ phase is produced in the same manner that was previously described, in which two out of every three {111}_B planes collapse to form double layers while the third plane remains stationary. However, as observed in Figure 5.16, two major differences distinguish the ω-B8₂ phase from the disordered ω-Ti phase: an ordered site occupancy in the unit cell and a c_ω lattice parameter that has doubled in length. The ordered structure shows Ti and Al atoms occupying two distinct sublattices at the 2d and 2c Wyckoff positions on the collapsed double layers and Ti, Nb, and Al randomly occupying the lattice sites on the stationary single layer at the 2a Wyckoff position. The ordered site occupancy results in the doubling of the c_ω-axis in the ω-B8₂ unit cell. Also shown in Figure 5.16 is that the length of the c_ω-axis corresponds to the full body diagonal of the BCC B2 unit cell, or a_B<111>_B.

A significant observation that can be made from Figure 5.16 is that the lattice sites in the ω-B8₂ structure are not fully inherited from the B2 phase, as would be the case if it were truly a displacive transformation. This indicates that some atomic movements are necessary in order to form the ω-B8₂ phase from the B2 phase. The transformation was examined by Bendersky et al. [37] and was shown to occur in steps that involved both displacive and replacive (atomic exchange between lattice sites) components. A purely displacive transformation from the B2 phase was shown
Figure 5.16. Shows the atomic site occupancies of the ordered β (B2) phase and the ω-B8₂ phase from the results of Bendersky et al. [37].

Ordered BCC β (B2) phase
- 1a Wyckoff Site: Ti
- 1b Wyckoff Site: Al and Nb

Hexagonal ω-B8₂ phase
- 2a Wyckoff Site: Random Ti, Nb, Al
- 2c Wyckoff Site: Al
- 2d Wyckoff Site: Ti
to produce an \(\omega\) phase, referred to as \(\omega'\), with trigonal \(P3m1\) symmetry. It was shown that the chemical order in this structure could occur by atomic movements that had no effect on the trigonal symmetry, which was then referred to as \(\omega''\). The chemical ordering that produced the \(\omega''\) structure was shown to have the proper site occupancy on the rumpled double layer as was determined on the planar double layer of the hexagonal \(\omega\)-B\(_{8}\) structure. This pertains to the 2c (Al) and 2d (Ti) Wyckoff positions of the \(\omega\)-B\(_{8}\) unit cell shown in Figure 5.16. Further atomic exchange between the single and double layers in the \(\omega''\) structure resulted in an increase in symmetry to the hexagonal \(\omega\)-B\(_{8}\) structure. This occurred by combining the 1a and 1b Wyckoff sites of \(\omega''\) to form the 2a Wyckoff site of \(\omega\)-B\(_{8}\) which were determined to have a random occupancy of Ti, Nb, and Al. Thus, the transformation of the B2 phase to the \(\omega\)-B\(_{8}\) phase can be viewed as traversing through an intermediate trigonal \(\omega''\) structure with both displacive and replacive components.

5.3.3.2 The Proposed \(\omega\)-D Phase

The \(\omega\)-D phase was shown to have several similarities to the \(\omega\)-related phases that indicated it transformed from the \(\beta\) phase by the same \(\{111\}_\beta\) plane collapse mechanism. This was determined from the orientation relationship in the form of diffuse electron scattering at 1/3\(\{111\}_\beta\) reflections which indicated that the \(\{0001\}_\omega\) planes of the \(\omega\)-D phase were parallel to the \(\{111\}_\beta\) planes of the \(\beta\) phase. Furthermore, the \(c_\omega\) lattice parameter of the \(\omega\)-D phase was determined from SAED patterns to be \(\sim 5.68\text{Å}\), or equivalent to the \(a_\beta <111>\_\beta\) body diagonal of the BBC unit cell. This is the same as the \(c_\omega\) lattice parameter that was observed by Bendersky et al. [37] and Strycor et al. [36] for the \(\omega\)-B\(_{8}\) phase and is twice that observed for the \(\omega\)-Ti phase. Furthermore, it was previously shown that the \(\omega\)-B\(_{8}\) phase has an
ordered structure with Ti and Al occupying lattice sites on the collapsed double layer and a random site occupancy on the single layer. Thus, these observations indicate that the ω-D phase also has an ordered structure.

In order to determine the site occupancy of the ordered ω-D phase it is necessary to first establish the total number of atoms within the hexagonal unit cell. This can be done by superimposing the unit cell of the ω-D phase onto that of the B2 phase using the orientation relationship that was previously determined. The schematic of the unit cell correspondence is shown in Figure 5.17 for the six layers of the \{111\}_h planes that correlate to the (0001)_ω planes. This figure also shows the \{1\overline{1}00\}_ω planes, which delineate the unit cell of the ω-D structure (seen as line traces), to be parallel to the \{1\overline{1}0\}_h planes. The site occupancy of the B2 structure is based on the conclusion reached in chapter 4 and shows Al occupying the 1a Wyckoff sites at (0,0,0) and Nb and Ti occupying the 1b Wyckoff sites at \((\frac{1}{2},\frac{1}{2},\frac{1}{2})\) in the BCC unit cell. The assessment of the two unit cells shows that there are 18 lattice sites, or atoms, in the B2 structure that convert to sites in a single unit cell of the ω-D phase.

The next step in the site occupancy determination is to investigate the correspondence between the lattice sites in the B2 phase and the ω-D phase. Figure 5.17 demonstrates what happens to the B2 sites when the \{111\}_h planes collapse occurs during a displacive transformation that involves no chemical ordering. If this occurs, then the resulting double layers of the ω-D structure will be occupied by Al atoms and Nb and Ti atoms on two separate sites and single layers that alternate between layers of Al atoms and Nb and Ti atoms on two separate sites as well. The problem with this arrangement is that the alternating single layers destroy the hexagonal symmetry and, thus, produce the trigonal symmetry.
Figure 5.17. The (111) projection of the B2 phase with the atomic site occupancy showing Nb and Ti atoms occupying the 1a Wyckoff site and Al atoms occupying the 1b Wyckoff site. (a) shows the planes at \( z = 0.0 \) Å (dark), 0.095 Å (light), and 0.189 Å (light); (b) shows the planes at \( z = 0.284 \) Å (dark), 0.379 Å (light), and 0.473 Å (light). The dashed lines denote the unit cell of the \( \omega \)-D phase.
In order to obtain hexagonal symmetry there must be atomic shuffling between atoms on the single and double layers during the B2 to \( \omega \)-D transformation. The most likely scenario based on the results of Bendersky et al. [37] would be for the sites on the double layers to be occupied solely by Ti and Al atoms as in the \( \omega \)-B\(_{82}\) structure. This would have to occur by the diffusion of Nb atoms from the double layers to the single layers and for Ti atoms from the single to the double layers.

Assuming that this occurred, then it is possible to determine the Wyckoff positions of the Ti and Al atoms on the double layers since it was determined that the \( \omega \)-D phase has \( \text{P6}_3/mcm \) symmetry. Using the tables of crystallography [64], it is found that the double layers consist of two 6g Wyckoff sites for each of the Ti and Al atoms. This means that 6 Ti atoms and 6 Al atoms are required to complete the ordering on the double layers, or in atomic percent 33%Ti and 33%Al (\# atoms on 6g site/\# atoms in unit cell) in the hexagonal \( \omega \)-D unit cell. The interesting correlation made from this assessment is that the composition of alloy 2 was determined to be 27Nb-33Ti-40Al (at.%) and, therefore, virtually the entire 33at.%Ti associated with the alloy composition goes to occupying the 6g sites of the \( \omega \)-D phase. This is based on the observation that the entire \( \beta \) matrix transformed to the \( \omega \)-D phase at low aging temperatures. Furthermore, the single layers must then be occupied mostly by Nb atoms and excess Al atoms (left over from the 6g site occupancy). Thus, the single layers, which contain 6 atomic sites, must be occupied by 27at.%Nb and \(~7\) at.%Al based on the alloy composition.

The site occupancies determined up to this point are still those that have been determined for the \( \omega \)-B\(_{82}\) phase which indicates that further ordering must have occurred in the \( \omega \)-D phase. The most likely occurrence for the further ordering would
be on the single layers that contain Nb and Al atoms. This is probable since the single layers of the $\omega$-B8$_2$ phase were determined to have a random occupancy of 50%Ti, 12.5%Al, and 37.5%Nb [37]. This equates to $\sim$79%Nb and $\sim$21%Al (after normalizing) for the single layers of the $\omega$-D phase. Therefore, if ordering occurred on the single layers as proposed, then it only involved Nb and Al atoms. Using this information and applying it to the crystallography tables of the P6$_3$/mcm space group, it can be shown that there are two Wyckoff positions, the 2b and 4d sites, that closely match the chemical composition of the single layers. This match is obtained if the 2b sites are occupied by two Al atoms and the 4d sites are occupied by four Nb atoms which give 11%Al and 22%Nb occupancy (in relation to the unit cell) on the single layers. These values are close to those which were determined from the alloy composition, 7at.%Al and 27at.%Nb.

A summary of the site occupancies previously determined is shown in Table 5.5. It shows that the single layers are comprised of 2b sites occupied by two Al atoms and 4d sites occupied by four Nb atoms. The double layers consist of two 6g sites that are occupied by six Ti atoms on one site and six Al atoms on the other site. The exact stoichiometry of the $\omega$-D phase determined from this site occupancy is 22Nb-33Ti-44Al (at.%), or Nb$_2$Ti$_3$Al$_4$. This agrees reasonably well with the composition of alloy 2 which was 27Nb-33Ti-40Al (at.%).

Finally, in order for the site occupancy to be correct, it must also be consistent with the observed symmetry restrictions, i.e. the 6$_3$ screw axis and the c-axis glide plane parallel to the $\{11\overline{2}0\}_c$ plane. However, both of these symmetry elements are accounted for by the site occupancy, as shown in the schematic of Figure 5.18. The six-fold symmetry requirement of the hexagonal crystal point group is observed for
Table 5.5. Proposed site occupancy for the \( \omega \)-D phase with \( \text{Ti}_3\text{Al}_4\text{Nb}_2 \) stoichiometry and \( \text{P6}_3/\text{mcm} \) (193) space group.

<table>
<thead>
<tr>
<th>Site Number</th>
<th>Site Position</th>
<th>Element</th>
<th>Wyckoff Position</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0 X 0</td>
<td>Al</td>
<td>2b</td>
</tr>
<tr>
<td>2</td>
<td>0 X 0.5</td>
<td>Al</td>
<td>2b</td>
</tr>
<tr>
<td>3</td>
<td>0.333 X 0.667</td>
<td>Nb</td>
<td>4d</td>
</tr>
<tr>
<td>4</td>
<td>0.667 X 0.333</td>
<td>Nb</td>
<td>4d</td>
</tr>
<tr>
<td>5</td>
<td>0.667 X 0.333</td>
<td>Nb</td>
<td>4d</td>
</tr>
<tr>
<td>6</td>
<td>0.333 X 0.667</td>
<td>Nb</td>
<td>4d</td>
</tr>
<tr>
<td>7</td>
<td>0.333 X 0.25</td>
<td>Ti</td>
<td>6g(_1)</td>
</tr>
<tr>
<td>8</td>
<td>0 X 0.333 0.25</td>
<td>Ti</td>
<td>6g(_1)</td>
</tr>
<tr>
<td>9</td>
<td>0.667 X 0.667</td>
<td>Ti</td>
<td>6g(_1)</td>
</tr>
<tr>
<td>10</td>
<td>0.667 X 0.75</td>
<td>Ti</td>
<td>6g(_1)</td>
</tr>
<tr>
<td>11</td>
<td>0 X 0.75</td>
<td>Ti</td>
<td>6g(_1)</td>
</tr>
<tr>
<td>12</td>
<td>0.333 X 0.333</td>
<td>Ti</td>
<td>6g(_1)</td>
</tr>
<tr>
<td>13</td>
<td>0.667 X 0.25</td>
<td>Al</td>
<td>6g(_2)</td>
</tr>
<tr>
<td>14</td>
<td>0 X 0.667 0.25</td>
<td>Al</td>
<td>6g(_2)</td>
</tr>
<tr>
<td>15</td>
<td>0.333 X 0.333</td>
<td>Al</td>
<td>6g(_2)</td>
</tr>
<tr>
<td>16</td>
<td>0.333 X 0.75</td>
<td>Al</td>
<td>6g(_2)</td>
</tr>
<tr>
<td>17</td>
<td>0 X 0.75</td>
<td>Al</td>
<td>6g(_2)</td>
</tr>
<tr>
<td>18</td>
<td>0.667 X 0.667</td>
<td>Al</td>
<td>6g(_2)</td>
</tr>
</tbody>
</table>

Note: 6g\(_1\) \( \rightarrow \) \( x = 0.333 \)

6g\(_2\) \( \rightarrow \) \( x = 0.667 \)
the (0001)\textsubscript{m} planes of the single layers at \( z = 0 \) and \( z = \frac{1}{2}c\textsubscript{m} \) in Figures 5.18a and 5.18b, respectively. Both of these layers show Al atoms at the unit cell corners surrounded by 6 Nb atoms. The double layers consisting of Ti and Al atoms at \( z = \frac{1}{4}c\textsubscript{m} \) and \( z = \frac{3}{4}c\textsubscript{m} \) provide evidence of the \( 6_3 \) screw axis. This is observed by focusing on the Ti atoms at \( z = \frac{1}{4}c\textsubscript{m} \) (Figure 5.17a) and then applying a translation of \( z = \frac{1}{2}c\textsubscript{m} \) along the \([0001]\textsubscript{m} \) direction with a 120° rotation that brings them into coincidence with the Ti atoms in the next layer at \( z = \frac{3}{4}c\textsubscript{m} \) (Figure 5.17b). Likewise, the c-glide plane is also observed in Figure 5.18 and is obtained by the symmetry operation that reflects specific atoms across the \{11\textsubscript{2}0\}\textsubscript{m} plane and translates it by a distance of \( c/2 \) along the c-axis. Thus, the site occupancy of the \( \omega \)-D phase is consistent with the observed symmetry requirements. It should be mentioned that this argument was fortuitous since the Wyckoff positions were obtained for the P6\textsubscript{3}mcm space group and, therefore, must incorporate the necessary symmetry restrictions.

It is now possible to show in Figure 5.19 the transformation of the B2 phase to the \( \omega \)-D phase using the site occupancy information previously determined. This figure demonstrates the displacive character of the transformation in which two out of every three \{111\}\textsubscript{p} planes (i.e. layers 1 and 2) collapse together and the third \{111\}\textsubscript{p} plane (layer 3) remains stationary to form the planar (0001)\textsubscript{m} plane of the \( \omega \)-D structure. If it is assumed that both phases possess their perspective stoichiometries (i.e. AB for B2 and \( A_4B_3C_2 \) for \( \omega \)-D phase), then it is possible that the atomic sites on the collapsed \{111\}\textsubscript{p} planes can be converted directly into sites on the planar double layers of the \( \omega \)-D structure without atomic diffusion. However, symmetry dictates that atoms occupying sites on the stationary \{111\}\textsubscript{p} planes must exchange positions.
Figure 5.18. The (0001) projection of the α-D phase which is based on the P6₃/mcm space group and Al₃Ti₅Nb₂ stoichiometry. (a) shows the single layer at \( z = 0.0 \)Å (dark) and double layers at \( z = 1/4c \) (light); (b) shows the single layer at \( z = 1/2c \) (dark) and double layers at \( z = 3/4c \) (light).
with their surroundings. Therefore, thermal activation must also be incorporated in
the transformation.

The ternary composition of alloy 2 is another reason why atomic shuffling
must have occurred during the B2 to \( \omega \)-D transformation. The stoichiometry of the
B2 phase with the ternary composition of alloy 2 would be \( A_4(B_{3.3}/C_{2.2}) \), where \( A = Al \),
\( B = Ti \), \( C = Nb \) and the parenthesis indicates random occupancy on one sublattice of
the B2 structure. There is only 40at.%Al in the alloy which means that the deficiency
in the occupancy of the 1a Wyckoff sites must be filled by Nb or Ti atoms. This isn't
critical, since the real problems occur for the random occupancy of Nb and Ti on the
1b Wyckoff site shown in Figure 5.19. The complications arise from the fact that Nb
atoms must be rejected from sites on the collapsed \{111\}_b planes at layers 1 and 5 and
exchanged with Al atoms on the stationary planes of layers 0 and 6. The vacated
sites then must be filled by Ti atoms from the stationary plane at layer 3.

Furthermore, Al atoms must also exchange with Nb or Ti atoms on layer 3 of the B2
structure in order to satisfy the 2b Wyckoff site occupancy requirement of the \( \omega \)-D
structure. Thus, the ordered \( \omega \)-D structure necessitates that atomic exchanges
between the \{111\}_b planes have to occur during its transformation from the B2 phase.

The atomic exchanges, however, do not imply that long range diffusion is
necessary for the transformation to occur. In fact, the diffusion path length must be
on the order of the unit cell dimension for the \( \omega \)-D phase, since the stoichiometry of
the unit cell is nearly the same as that of the alloy 2 composition. This partly
explains why the \( \omega \)-D phase can transform from the B2 phase at low temperatures
even though long range diffusion does not occur. This was verified in Figure 5.11
which showed that APDBs were still present in the B2 matrix after the heat
Ordered BCC β (B2) phase
- 1a Wyckoff Site: Al
- 1b Wyckoff Site: Ti and Nb

Ordered ω-D phase
- 2b, 6g Wyckoff Sites: Al
- 6g Wyckoff Site: Ti
- 4d Wyckoff Site: Nb

Figure 5.19. Shows the atomic site occupancies of the B2 phase and the ω-D phase.
treatment at 400°C for 12 hours. In this case, the APDBs had formed in the as-cast microstructure prior to the heat treatment. Thus, the high number density of fine ω-D precipitates that transformed in the as-cast microstructure simply coarsened during the 400°C heat treatment.

5.3.4 Crystallographic Aspects of the ω-D Phase Transformation

The results of this study indicated that the transformation of the ω-D phase from the B2 phase could be described crystallographically as a series of transitions that involved symmetry. This type of description was previously covered in chapter 2 and was based on the study by Bendersky et al. [37]. It was shown in Figure 2.11 of chapter 2 that the transformation of the ω-B8₂ phase from the disordered β phase occurred by a sequence of transitions that crossed a state of minimum symmetry, which was the ω"-P3m1 space group. It was also shown that the individual transitions of the transformation were connected together by subgroup/supergroup relations in crystallography. Thus, the purpose of this section is to show that the transformation of the ω-D phase occurred by a similar series of transitions, except that the last transitions of the ω-D phase were different from the ω-B8₂ phase.

The transformation of the ω-D phase was previously shown to have occurred after the β phase ordered to the B2 phase. Therefore, the first series of transitions that occurred for the ω-D phase were similar to those for the ω-B8₂ phase based on subgroup/supergroup relations [64]. These initial transitions are described using the space group and phase notations:

\[ \text{Im} \bar{3} \text{m(β)} \rightarrow \text{Pm} \bar{3} \text{m(B2)} \rightarrow \text{R} \bar{3} \text{m} \rightarrow \text{P} \bar{3} \text{m1(ω")}, \]

where ω" is the low symmetry trigonal phase that has undergone some degree of chemical ordering on the collapsed double layers [37]. The physical description given
to these transitions is as follows: the $\text{Im}3\text{m}$ to $\text{Pm}3\text{m}$ transition involved chemical ordering in the $\beta$ matrix that produced two translational variants of the B2 phase from the disordered $\beta$ phase; the $\text{Pm}3\text{m}$ to $\text{R}3\text{m}$ transition determined which one of the four possible body diagonals in the B2 unit cell became the $\overline{3}$ axis of the trigonal $\omega''$ phase; and the $\text{R}3\text{m}$ to $\text{P}3\text{m}1$ transition determined which one of the three possible $\{111\}B$ planes remained stationary, while the two other planes collapsed together. Thus, the structural changes that occurred in these three transitions were those that produced the $\omega$ characteristics in the $\omega$-D phase.

Once that the $\omega''$-$\text{P}3\text{m}1$ phase was formed, the remaining transformation that formed the $\omega$-D phase could have occurred by two different transition paths. The two paths are shown in the schematic of Figure 5.20. In this schematic, the order parameter, which is seen as the bracketed numbers, indicates how many variants of the product phase will be formed and the directions of the arrows show whether there will be an increase or a decrease in the symmetry of the product phase. The first transition path was based on the results published by Bendersky et al. [37] that showed three translational variants of an $\omega$-related phase that had precipitated from the coarse $\omega$-$\text{B}8_2$ domains in a 700°C aged sample of the Ti$_4$Al$_3$Nb alloy. The $\omega$-related phase that was observed in the study by Bendersky et al. was similar to the $\omega$-D phase that was observed in this study, since both phases had similar lattice parameters. The $\omega$-$\text{B}8_2$ phase was shown in the earlier study by Bendersky et al. to have formed from a matrix consisting of the $\omega''$-$\text{P}3\text{m}1$ phase in the Ti$_4$Al$_3$Nb alloy. The second transition path shown in Figure 5.20 is proposed based on the results of this study. This path shows that an intermediate trigonal $\text{P}3\text{m}1$ ($\omega'''$) phase formed that possessed a minimum in symmetry compared to the $\omega''$-$\text{P}3\text{m}1$ phase and the $\omega$-D
Figure 5.20. Shows the transformation paths from the $\beta$ phase to the $\omega$-D phase described by subgroup/symmetry relations.
phas e. Thus, it was possible that the $\omega$-D phase could have transformed along both of
the paths shown in Figure 5.20.

The result showing the $1/3\{011\}_p$ reflections in the SAED patterns of the B2
matrix in the as-cast RAM sample was found to be consistent with the second path in
Figure 5.20. This result indicated that the chemical ordering that formed the $\omega$-D
phase had occurred in the very early stages of the $\omega$ nucleation process. However, in
the Ti$_4$Al$_3$Nb alloy studied by Bendersky et al. [37], it was shown that a 400°C/min.
cooling rate caused the transformation of the high temperature $\beta$ phase completely to
the $\omega''$ phase. The 400°C/min. cooling rate was much slower than that of the as-cast
RAM sample of alloy 2, which contained a high number density of small $\omega$-related
precipitates distributed homogeneously in the B2 matrix as shown in Figure 4.3.
Thus, it was expected that the $\omega''$ phase should have formed in the as-cast RAM
sample, since the $\omega''$ phase involves the least amount of chemical ordering and the
partial collapse of the double layers compared to the $\omega$-D phase. However, the small
$\omega$-related precipitates in the B2 matrix of the as-cast RAM sample showed reflections
located at the $1/3\{011\}_p$ positions in the SAED pattern of Figure 4.5. These were
$\{1\overline{1}00\}_p$ reflections of the $\omega$-D phase which indicated that further ordering over that of
the $\omega''$ had already occurred in the small $\omega$-related precipitates. This was surprising
since the limited time that was available for these precipitates to form should have
prevented the complete collapse of the double layers, which was necessary to form the
HCP symmetry of the $\omega$-D phase.

The result showing no triple point junctions for the interfaces observed in the
coarse $\omega$-D domains was consistent with the second path shown in Figure 5.20. This
conclusion was based on the number of variants that would have formed and,
depended on the transformation path that was taken. If the first path had occurred, then three translational variants of the $\omega$-D phase would have formed from the intermediate $\omega$-B$_8$$_2$ domain, since the order parameter of the last transition was three. The three translational domains can be visualized using the schematic shown in Figure 5.18 by translating the Al atom at the origin of the unit cell by \(1/3<1\overline{1}00>\) into the two positions occupied by Nb atoms, which are on the 4d Wyckoff sites in the zero layer of the (0001)$_w$ plane. If the second path had occurred, then by the same argument it would have been expected that two translational variants of the $\omega$-D phase would have formed from the intermediate trigonal $\omega''$-P$3\overline{1}$m phase. This path agrees with the observations of the 600°C aged sample shown in Figure 5.14, which showed that the single rotational variants of the coarse $\omega$-D domains contained wavy interfaces that did not intersect each other. This observation was consistent with the presence of two translational variants separated by the interface.

The tables of crystallography indicated that the $\omega''$ was formed by chemical ordering that occurred in the $\omega''$ phase. The P$3\overline{1}$m space group of the $\omega''$ phase is listed as a type IIb maximal non-isomorphic subgroup of the $\omega''$-P$3\overline{1}$m space group. The ordering caused an increase in the lattice parameters of the $\omega''$ phase which made the unit cell the same size as that of the $\omega$-D phase, and rotated the 2/m mirror symmetry axis by 90° from the $<1\overline{1}20>$ direction in the $\omega''$ phase, as compared to the $<1\overline{1}00>$ direction in the $\omega''$ phase. This rotation caused the 2/m symmetry axis in the $\omega''$-P$3\overline{1}$m phase to become parallel to the 2/m symmetry in the $\omega$-D phase, which had the P$6_3$/mcm space group. This chemical ordering was associated with the single layers, since it was previously shown that ordering occurred between Al and Nb atoms on the single layers of the $\omega$-D phase. The Wyckoff sites on the single layers of
the $\omega''$ phase that were consistent with this ordering scheme were the 1a site at $(0, 0, 0)$; the 1b site at $(0, 0, \frac{1}{2})$; the 2c site at $(\frac{1}{3}, \frac{1}{3}, 0)$ and $(\frac{2}{3}, \frac{2}{3}, 0)$; and the 2d site at $(\frac{1}{3}, \frac{2}{3}, \frac{1}{2})$ and $(\frac{2}{3}, \frac{1}{3}, \frac{1}{2})$. Thus, the ordering occurred between atoms on the 1a and 2c sites in the $z = 0$ layer and atoms on the 1b and 2d sites in the $z = \frac{1}{2}$ layer. This would have increased the lattice parameters of the $\omega''$ phase to the same size as those of the $\omega$-D phase. The low symmetry of the $\omega''$ phase indicated that the atomic occupancy of these sites was general. The only restriction on the atomic site occupancy would have been that dissimilar atoms had to occupy the two types of Wyckoff sites on each single layer. The Wyckoff sites that were consistent with the double layers of the $\omega''$ phase were the 6k$_1$ and 6k$_2$ sites. The 6k sites accounted for the partial collapse of the double layers in the $\omega''$ phase, since the $z$-parameter in the Wyckoff coordinates of these sites was variable.

The advantage to forming the trigonal $\omega''$ phase, as opposed to the $\omega$-B8$_2$ phase, as the intermediate transitional phase was that the formation of this phase involved very little modification to the site occupancy and the incomplete collapse of the double layers as compared to the $\omega''$ phase. In comparison, the transition path that formed the $\omega$-B8$_2$ phase involved an increase in symmetry which would have required considerably more atomic exchanges between the single and double layers, and the complete collapse of the double layers. The transition from the $\omega''$ phase to the $\omega$-B8$_2$ phase would have also required thermal energy, since Bendersky et al. [37] showed that this transition occurred after heat treating the Ti$_4$Al$_2$Nb alloy for 26 days at 700°C or cooling slowly from 1100°C at ~400°C/minute. This result indicated that the cooling rate associated with the as-cast RAM sample of alloy 2 would have been too fast for the transition of the $\omega$-B8$_2$ phase to have occurred. Thus, it was more
likely that the small precipitates that formed in the B2 matrix of the as-cast RAM sample consisted of the \( \omega'' \) phase.

The final transition from the \( \omega'' \) phase to the \( \omega-D \) phase was expected to require thermal energy since exchanges between Nb and Al atoms on the single layers were necessary. The site occupancy of the B2 phase that was initially inherited in the P\( \overline{3} \)1m structure of the \( \omega'' \) phase would have produced Al rich single layers with the 1a and 2c sites and Nb and Ti rich single layers with the 1b and 2d sites. Thus, the Al and Nb atoms would have had to exchange sites between the two single layers. However, this represented the longest path between sites in the unit cell and the exchange would have had to pass through the double layers. These exchanges were necessary to form the \( \omega-D \) structure since the single layers in this structure have the same Al and Nb content. Therefore, it was expected that the \( \omega-D \) phase was able to only form during furnace cooling from the \( \beta \) phase at 1400\( ^\circ \)C or during isothermal heating at 600\( ^\circ \)C for 12 hours.
CHAPTER 6
THE ORTH(HEX) PLATES

6.1 Introduction

In chapter 4, it was shown (see Figures 4.8, 4.9, and 4.11) that lenticular precipitates (referred to as plates) formed in the BCC β phase of 27Nb-33Ti-40Al (alloy 2) and that composition and cooling rate affected their formation. The effect of composition was observed by the presence of plates in the interdendritic regions of the as-cast sample which indicated that the composition in these regions must have been conducive for the nucleation of the plates to occur. The effect of cooling rate was observed in the levitated and drop quenched sample by the presence of a high number density of plates throughout the β matrix. This type of microstructure was also observed in the heat treated samples of alloy 2 that were water quenched. Thus, these observations indicated that a fast cooling rate favored the formation of the plates from the β phase, while a slow cooling rate favored the formation of either the ω-D phase (intermediate cooling rate) or the equilibrium σ and γ phases (very slow cooling rate).

The purpose of this chapter is to examine the formation of plates from the β phase in greater detail. Results concerning the structure, the shape morphology, and the orientation relationship of the plates with respect to the β phase will be presented. This will be followed by a discussion of the transformation mechanism and will be treated in terms of a displacive transformation using a group/subgroup representation and the invariant line concept.
6.2 Results

The investigation of plates that formed in samples during rapid cooling from high temperatures revealed two closely related phases, which were based on the orthorhombic (ORTH) and the hexagonal close packed (HCP) Bravais structures. The results indicated that the ORTH structure was the most prevalent phase. The HCP structure was found only in thick plates of the 1300°C heat treated sample, however, plates with the ORTH structure were also observed in this sample. The results showed that several variants of the ORTH structure existed and were dependent on plate thickness. In addition, the lattice parameters for these ORTH phases were affected by the heat treatment temperatures. Therefore, a total of three different ORTH phases and one HCP phase (some containing a third phase) were identified from the correlation of plate thickness with heat treatment temperature in this study.

This study also revealed that the plates contained a variety of planar defect structures including anti-phase domain boundaries (APDBs). However, there were significant differences between the APDBs of the ORTH and HCP plates.

Thus, the results are divided into four sections that deal with the structural analysis of the plates, determination of the plate morphology, zig-zag plate morphology, and internal defect structural analysis of the plates. The orientation relationship is also included since it contains information regarding the rigid body rotation between the plates and the β phase. This information was used to distinguish between the HCP and the ORTH phases.
6.2.1 Structural Analysis

The structural analysis of the plates is divided into three sections: thick plates with the HCP phase, medium thick plates with the ORTH1 phase, and thin plates with the ORTH2 and ORTH3 phases. In each of these sections, the results pertinent to the determination of the crystal structure, lattice parameters, orientation relationship with the β phase, and habit plane of the plates is described.

6.2.1.1 Thick Plates with HCP Structure

It was determined that plates with cross-sections typically ≥0.15µm possessed the HCP crystal structure. Some of these plates were found to have a complicated structure due to the presence of another phase in addition to the HCP phase. However, both types of thick plates were only observed in the 1300°C heat treated and water quenched sample. As was described in chapter 4, this heat treatment resulted in the formation of the σ phase at 1300°C and the subsequent formation of the plates from the β phase during rapid cooling. The microstructure displaying the distribution of these three phases was shown previously in Figure 4.11b. In the subsequent analysis of this sample, it was found that the thick HCP plates preferentially formed next to σ grains and often were connected to σ grains. Plates that had the ORTH phase were also observed in this heat treated sample, however, these plates were located away from the σ grains and had cross-section thicknesses of ≤0.15µm.

Several characteristics of the thick plates are shown in the TEM micrograph and SAED pattern of Figure 6.1. The plate observed in the micrograph of Figure 6.1a was determined to have a thickness of ~0.16µm. The SAED pattern of Figure 6.1b showed that the plate formed from the β phase with the Burgers orientation
Figure 6.1. Shows a thick plate with the HCP structure observed in the 1300°C aged sample. (a) TEM micrograph of the HCP plate; (b) SAED pattern of the orientation relationship observed between the HCP plate and the β phase, which was [0001]$_H$ $\parallel$ [011]$_β$ and (1000)$_H$ $\parallel$ (2T1)$_β$. 
relationship [93]:

\[[0001]_H \parallel [011]_\beta \quad \text{and} \quad (11\overline{2}0)_H \parallel (\overline{1}1\overline{1}1)_\beta.\]

This orientation relationship can be observed in Figure 6.2 with the stereographic projection of the \([0001]_H \parallel [011]_\beta\) poles. From this orientation relationship, twelve variants of the HCP plates were formed from the \(\beta\) phase. Six variants were produced by aligning the \([0001]_H\) direction parallel to the six possible \(<011>\_\beta\) directions and the other six additional variants by aligning the \((11\overline{2}0)_H\) planes parallel to the two possible \(\{\overline{1}1\overline{1}1\}_\beta\) planes present at each \(<011>_\beta\) direction. The diffraction pattern also showed the \((1\overline{1}00)_H\) and \((2\overline{1}11)_H\) reflections to be parallel and the \((011)_\beta\) and \((T010)_H\) reflections to be separated by an angle of 5.50° (±0.20°).

The HCP structure of the thick plates was confirmed by CBED analysis. This is demonstrated in Figure 6.3 using CBED patterns to show the 6-fold symmetry of the \([0001]_H\) zone axis. Two orthogonal mirror lines are also observed in these CBED whole patterns using a large camera length (Figure 6.3a) and a small camera length (Figure 6.3b). The presence of the mirror lines and the 6-fold axis indicate that these CBED whole patterns have 6mm symmetry. The symmetry of the whole pattern shown in Figure 6.3b was determined by faint HOLZ lines, since outer HOLZ rings were never observed even after long exposure times. The 6mm symmetry indicates that the HCP phase belongs to the 6mm1\(\text{H}\) projection diffraction group, as shown in Table 6.1. There are two possible diffraction groups showing the 6mm symmetry in the CBED whole patterns: 6mm or 6mm1\(\text{H}\). In either case, both of these diffraction groups are consistent with the HCP crystal structure.

The point group of the HCP plates was determined by using a second zone axis of higher symmetry, or the \([1\overline{1}2\overline{6}]_H\) zone axis in this study, and is shown in
Figure 6.2. The stereographic projection of the orientation relationship between the HCP phase and the β phase which shows the [0001]_H // [011]_β poles.
Figure 6.3. CBED patterns showing the whole pattern symmetry of the [0001]_H zone axis observed for the thick HCP plates. (a) a large camera constant; (b) a small camera constant.
Table 6.1. Shows the relation between the possible diffraction groups and the symmetries observed in the Convergent Beam Electron Diffraction (CBED) patterns of the HCP phase at the [0001]$_{H}$ zone axis. [89].

<table>
<thead>
<tr>
<th>Observed Symmetry in Whole Pattern</th>
<th>Projection Diffraction Group</th>
<th>Possible Diffraction Groups</th>
<th>Whole Pattern Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>6mm</td>
<td>6mm$R$</td>
<td>$6m_Rm_R$</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>6mm</td>
<td>6mm$R$</td>
<td>6mm</td>
</tr>
<tr>
<td></td>
<td>$6_Rmm_R$</td>
<td>6mm$R$</td>
<td>3m</td>
</tr>
<tr>
<td></td>
<td>6mm$R$</td>
<td>6mm$R$</td>
<td>6mm</td>
</tr>
</tbody>
</table>
Figure 6.4. These CBED whole patterns showed a 2-fold symmetry with two orthogonal mirror lines, or 2mm symmetry, using a large camera length (Figure 6.4a) and a small camera length (Figure 6.4b). The 2mm symmetry of these CBED whole patterns are consistent with the 2mm1R projection diffraction group, as shown in Table 6.2. The 2m$_R$m$_R$ and 2$_R$mm$_R$ diffraction groups are eliminated since they do not show a 2mm symmetry in the whole pattern. This leaves the 2mm or 2mm1$_R$ symmetries as the possible diffraction groups.

The final step in the determination of the point group consisted of combining the results of the [0001]$_H$ and [1126]$_H$ zone axes. A compiled list from Buxton et al. [91] of all the possible point groups for each of the four possible diffraction groups is shown in Table 6.3. The examination of the table showed that there was only one point group that occurred from the diffraction groups of both zone axes. This was determined to be the 6/mmm point group. Since there were no other point groups that met this criterion, then this must be the point group of the HCP phase.

The space group of the HCP phase was determined by the presence of additional translational symmetry elements, i.e. a screw axis and/or glide plane. This study examined the [1100]$_H$ and [1120]$_H$ zone axes and was conducted on a number of plates. Figure 6.5 shows a CBED whole pattern of the [1120]$_H$ zone axis. This pattern shows that the (0001)$_H$ reflection which is kinematically forbidden does have limited intensity due to dynamical double diffraction effects. Very diffuse dark lines running normal and parallel to the $g=(0001)_H$ reflection were also discernable in these disc's. These lines were interpreted as black crosses known as Gjonnes-Moodie lines or G-M lines [89]. These black crosses indicated that a screw axis lied parallel to the c-axis and that a glide plane lied parallel to the zone axis and was contained in the
Figure 6.4. CBED patterns showing the whole pattern symmetry of the [1126]_H zone axis observed for the thick HCP plates. (a) a large camera constant; (b) a small camera constant.
Table 6.2. Shows the relation between the possible diffraction groups and the symmetries observed in the Convergent Beam Electron Diffraction (CBED) patterns of the HCP phase at the [112\bar{6}]_{H} zone axis. [89].

<table>
<thead>
<tr>
<th>Observed Symmetry in Whole Pattern</th>
<th>Projection Diffraction Group</th>
<th>Possible Diffraction Groups</th>
<th>Whole Pattern Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>2mm</td>
<td>2mm1_{R}</td>
<td>2m_{R}m_{R}</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>2_{R}mm_{R}</td>
<td>m</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2mm1_{R}</td>
<td>2mm</td>
</tr>
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</table>
Table 6.3. Shows the relation between diffraction groups and crystal point groups for the CBED patterns of the HCP plates. [89].

<table>
<thead>
<tr>
<th>Zone Axis</th>
<th>Diffraction Groups</th>
<th>Crystal Point Groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>[0001]</td>
<td>6mm</td>
<td>6mm</td>
</tr>
<tr>
<td></td>
<td>6mm1_R</td>
<td>6/mmm</td>
</tr>
<tr>
<td>[1126]</td>
<td>2mm</td>
<td>mm2, 6m2</td>
</tr>
<tr>
<td></td>
<td>2mm1_R</td>
<td>mmm, 4/mmm, 6/mmm, m3, m3m</td>
</tr>
</tbody>
</table>
Figure 6.5. CBED pattern showing the diffuse black cross in the (0001) disc observed in the [11\overline{2}0]_H zone axis of the HCP plates.
c-axis. The only possible space group that was consistent with these observations was P6₃/mmc [89,91].

Occasionally boundaries were observed to run across the HCP plates. Figure 6.6a shows a plate that contains such a boundary. Figure 6.6b shows the SAED pattern from a region containing this boundary and it does not indicate the presence of two differently oriented crystals. Further tilting of the specimen consistently confirmed the existence of one single pattern that was consistent with the HCP phase. However, analysis of the CBED patterns from the two sides (A and B shown in Figure 6.7a) of the boundary revealed the existence of possibly another phase in addition to the HCP phase. The CBED pattern shown in Figure 6.7a confirms that the A side had 6mm symmetry, which was consistent with the [0001]ₜ zone axis of the HCP phase. However, the CBED pattern shown in Figure 6.7b reveals that the B side had 3m symmetry. From Buxton et al. [91], the possible diffraction groups showing 3m symmetry in the CBED whole pattern are 6ₘₘₘₚ, 3ₘₚ, and 3m. None of these diffraction groups are possible for the HCP phase. Thus, this new phase must have either the cubic or trigonal Bravais lattice since only they are consistent with the 6ₘₘₘₚ, 3ₘₚ, and 3m diffraction groups. Since the tilting of the specimen did not reveal any other diffraction patterns beside the one for the HCP, then it was concluded that the phase existing on the B side had a trigonal lattice which can result in an identical SAED pattern as one belonging to an HCP phase.

The lattice parameters of only the HCP phase were determined in this study and were obtained from SAED patterns of the [0001]ₜ and [1120]ₜ zone axes:

\[ aₜ = 5.792\text{Å} \pm 0.026\text{Å} \]  
\[ cₜ = 4.625\text{Å} \pm 0.016\text{Å} \]

The \( aₜ \) and \( cₜ \) lattice parameters
Figure 6.6. Shows the boundary observed in a thick HCP plate. (a) TEM micrograph; (b) SAED pattern of the two regions separated by the boundary which was consistent with the orientation relationship observed between the HCP plates and the β phase.
Figure 6.7. CBED patterns of the two sides (A and B in Figure 6.6). (a) shows the 6mm symmetry that was consistent with the [0001]_H zone axis of the HCP phase; (b) shows the 3m symmetry of possibly a different phase.
were calculated from measurements of the d-spacings for \( \{\overline{1}00\}_H \) and \( (0001)_H \) reflections, respectively.

The habit plane of these thick plates was obtained at the \([0001]_H \parallel [011]_\beta\) orientation. It was observed that plates were oriented edge-on when viewed in the \([0001]_H \parallel [011]_\beta\) direction, but were inclined slightly when viewed in the \([1\overline{1}20]_H \parallel [\overline{1}1\overline{1}]_\beta\) direction. This is demonstrated by comparing the plate morphology shown previously in Figure 6.1a at the \([011]_\beta\) zone axis to that shown in Figure 6.8a at the \([\overline{1}1\overline{1}]_\beta\) zone axis. The interface between the plate and the \(\beta\) phase at the \([011]_\beta\) zone axis showed no overlap in the projected image, which indicated that the plate was oriented edge-on relative to the electron beam direction. The normal to this interface, or habit normal, showed that it lied \( \sim 10^\circ \) \((\pm 1')\) from the \( (2\overline{1}1)_\beta \) plane normal towards the \( (1\overline{1}1)_\beta \) plane normal direction. When the plates were observed at the \([\overline{1}1\overline{1}]_\beta\) zone axis, as is the plate shown in Figure 6.8a, the plate/\(\beta\) phase interface was always parallel to the \( (2\overline{1}1)_\beta \) planes and inclined relative to the beam direction. This is observed in the micrograph of Figure 6.8a as two parallel traces of the interface which intersect the top and bottom of the thin foil along both sides of the plate. The amount of inclination was determined by tilting the plate about the \( g = (0001)_H \) reflection until the interface was oriented edge-on and then measuring the tilt from the goniometer. The results of this experiment are shown in the micrograph of Figure 6.8b and indicate that the amount of tilt measured from the \([\overline{1}1\overline{1}]_\beta\) zone axis correlates with the angle measured between the habit normal and the \( (2\overline{1}1)_\beta \) plane normal from Figure 6.1a. Therefore, applying this method to a number of thick HCP plates showed that the habit plane normal was \( 10^\circ \) \((\pm 1')\) from the \( (2\overline{1}1)_\beta \) plane normal.
Figure 6.8. TEM micrographs of a thick HCP plate. (a) shows the plate inclined, relative to the beam, at the [T1T]p zone axes; (b) shows the plate edge-on after tilting ~11° along the g = (011)p || (000)H reflections.
6.2.1.2 Medium Thick Plates with the ORTH1 Structure

The results indicated that plates with thicknesses of $0.05 \mu m \leq t \leq 0.15 \mu m$ possessed the orthorhombic (ORTH) structure. The lattice parameter of this phase depended on the heat treatment, as will be shown in the following section. Since the diffraction pattern of this phase was different than the ORTH phase observed in thin plates, the thicker plates were referred to as ORTH1. In addition, many of the characteristics observed for the ORTH1 plates were similar to the HCP plates, including the number of plate variants derived from the same type of orientation relationship with the $\beta$ phase.

The plates with the ORTH1 phase were observed in the RAM samples heated at 1300°C, 1400°C, and 1500°C and the EM levitated samples. The SAED patterns of these plates were indistinguishable from those of the thick HCP plates. However, the CBED analysis showed that they possessed orthorhombic, and not hexagonal, symmetry.

Figure 6.9 shows micrographs of a medium thick plate that had a thickness of ~0.065 µm (650Å) and the diffraction characteristics of the ORTH1 phase. The SAED pattern of Figure 6.9b was indexed with the \( [001]_{\text{O1}} \) direction parallel to the \( [011]_{\beta} \) direction and the \( (110)_{\text{O1}} \) planes parallel to the \( (2\overline{1}1)_{\beta} \) planes and showed the orientation relationship:

\[
[001]_{\text{O1}} \parallel [011]_{\beta} \quad \text{and} \quad (110)_{\text{O1}} \parallel (2\overline{1}1)_{\beta}.
\]

This orientation relationship indicates that twelve variants were formed during the transformation. Six variants were formed by aligning the \( [001]_{\text{O1}} \) direction parallel to six possible \( <011>_{\beta} \) directions and six more variants were formed by aligning the \( (110)_{\text{O1}} \) planes parallel to either of two \( (2\overline{1}1)_{\beta} \) planes at each \( <011>_{\beta} \) direction.
Figure 6.9. Shows a medium thick plate with the ORTH1 structure. (a) TEM micrograph; (b) SAED pattern of the orientation relationship between the ORTH1 plate and the β phase, which was [001]₀₁ || [011]ₜ and (110)₀₁ || (211)ₜ.
The stereographic projection of Figure 6.10 demonstrates that the above crystallographic relationship also includes coincidences of two other directions between the ORTH1 and β phase. It shows the [001]₀₁ || [011]ᵦ poles and the additional orientation relationship:

\[ [110]₀₁ || [\overline{1}1\overline{1}]ᵦ \text{ and } (001)₀₁ || (011)ᵦ. \]

The analysis of the orientation relationship observed in the SAED pattern of Figure 6.9b showed that the angular relationship between the (130)₀₁ plane of the ORTH1 phase and the (\overline{1}1\overline{1})ᵦ plane of the B2 phase was affected by the heat treatment temperature. It was found that the plates which formed during water quenching from 1300°C showed that the (130)₀₁ planes were parallel to the (\overline{1}1\overline{1})ᵦ planes. Thus, the orientation relationship observed for these plates was exactly the same in appearance as that observed for the HCP plate shown in Figure 6.1b. This result was different than that which was observed for the ORTH1 plates that formed during water quenching from ≥1400°C. The orientation relationship observed for these ORTH1 plates showed that the (130)₀₁ planes were rotated slightly from the (\overline{1}1\overline{1})ᵦ planes. This rotation was due to the distortions in the a-axis and b-axis lattice parameters of the orthorhombic structure compared to those of the HCP structure. The relationship between the orthorhombic and HCP structures will be covered in the discussion section.

The CBED analysis showed that crystal structure of the ORTH1 plates was consistent with the orthorhombic symmetry. Figure 6.11 shows a CBED pattern obtained from the same plate previously shown in Figure 6.9. This CBED whole pattern showed that the intensity of the (020)₀₁ reflection was greater than that of the (110)₀₁ and (1\overline{1}0)₀₁ reflections. This result indicated that the symmetry of this
Figure 6.10. The stereographic projection of the orientation relationship between the ORTH1 phase and the β phase which shows the [001]_ORTH1, [011]_β poles.
Figure 6.11. CBED pattern showing the whole pattern symmetry of the \( [001]_{01} \) zone axis observed for the ORTH1 plates.
CBED pattern was 2mm, since it showed a 2-fold symmetry with two orthogonal mirror lines. Thus, it was determined from Table 6.4 that the 2mm1_\text{r} projection diffraction group was consistent with the 2mm symmetry of the whole pattern. From this projection group, there were two possible diffraction groups that were consistent with the 2mm symmetry: the 2mm and the 2mm1_\text{r}.

The ORTH1 phase was also studied at the [110]_01 zone axis in order to determine the point group. Figure 6.12a shows the CBED whole pattern of the [110]_01 zone axis which was found to have 2mm symmetry. These observations and the use of Table 6.4 indicate that the two possible diffraction groups were the same as determined for the [001]_01 zone axis. This information was compiled in Table 6.5 to facilitate the determination of the crystal point groups for the ORTH1 phase. All possible point groups based on hexagonal, cubic, and tetragonal Bravais structures were eliminated from this table, since no orientations were found that showed 6-fold, 3-fold, or 4-fold axes for the ORTH1 phase. Thus, there were only three possible point groups remaining: mm2, 222, and mmm [91]. In order to determine whether a mirror plane existed perpendicular to the c-axis, as in the mmm point group, an ORTH1 plate was tilted from the [110]_01 zone axis along the (001)_01 reflection to form a systematic row of reflections as shown in Figure 6.12b. This procedure eliminated the problems due double diffraction at the [110]_01 zone axis which may cause intensity to be seen for the forbidden reflections, for example the double diffraction for the (001)_01 reflection can occur between the (111)_01 and (110)_01 reflections. The results of this tilting procedure indicated that reflections at odd numbered (00l) positions disappeared, and that only even numbered (00l) reflections remained visible. This meant that the (001)_01 reflections were forbidden and indicated that a
Table 6.4. Shows the relation between the possible diffraction groups and the symmetries observed in the Convergent Beam Electron Diffraction (CBED) patterns of the ORTH1 phase at the [001]₀ and the [110]₀ zone axes. [89].

<table>
<thead>
<tr>
<th>Observed Symmetry in Whole Pattern</th>
<th>Projection Diffraction Group</th>
<th>Possible Diffraction Groups</th>
<th>Whole Pattern Symmetry</th>
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<tr>
<td>2mm</td>
<td>2mm₁₀</td>
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<tr>
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Figure 6.12. The structural analysis of the medium thick ORTH1 plates. (a) CBED pattern showing the 2mm whole pattern symmetry of the [110]₀₁ zone axis; (b) SAED pattern obtained by tilting the thin foil specimen from the [110]₀₁ zone axis along the \( g = (001) \) reflection.
Table 6.5. Shows the relation between the diffraction groups and crystal point groups for the CBED patterns of the ORTH1 plates. [89].

<table>
<thead>
<tr>
<th>Zone Axes</th>
<th>Diffraction Groups</th>
<th>Crystal Point Groups</th>
</tr>
</thead>
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<tr>
<td>[001] and [110]</td>
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</tr>
<tr>
<td></td>
<td>2m&lt;sub&gt;R&lt;/m&gt;&lt;sub&gt;R&lt;/sub&gt;</td>
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<tr>
<td></td>
<td>2mm&lt;sub&gt;1&lt;/sub&gt;&lt;sub&gt;R&lt;/sub&gt;</td>
<td>mmm</td>
</tr>
<tr>
<td></td>
<td>m&lt;sub&gt;1&lt;/sub&gt;&lt;sub&gt;R&lt;/sub&gt;</td>
<td>mm2</td>
</tr>
</tbody>
</table>
mirror plane existed perpendicular to the c-axis, which was consistent with the mmm point group. Thus, this result combined with those showing that the (010) and (100) reflections were also forbidden indicated that the ORTH1 phase has a base-centered orthorhombic Bravais lattice with the mmm point group. This suggested that the ORTH1 phase had the Cmmm point space group if no other symmetry elements, such as a screw axis and/or glide plane, were present.

The [100]₀₁ zone axis was examined by CBED analysis in order to verify whether the ORTH1 phase had the same Cmcm space group as the O-Ti₂AlNb phase [13]. The [100] zone axis of this space group would contain evidence of the 2₁ screw axis in the [001] direction and the c-glide plane parallel to the (010) planes as a black cross in kinematically forbidden (001)₀₁ reflections [89]. The results of this CBED analysis did not detect the black cross in the ORTH1 plates. However, this analysis was complicated as a result of the thin cross-section of the ORTH1 plates and the projection problems that these plates had with the surrounding B2 matrix at the [100]₀₁ zone axis. These problems were exaggerated by the fact that dynamical diffraction conditions must be met to ensure the proper conditions for forming the black cross [89], which meant that the plates present in thick areas of the thin foil had to be analyzed.

The lattice parameters of the ORTH1 phase were determined from SAED patterns at the [001]₀₁ and [110]₀₁ zone axes. The a₀₁, b₀₁, and c₀₁ lattice parameters were calculated from the d-spacing measurements of the (200)₀₁, (020)₀₁, and (002)₀₁ reflections, respectively. Table 6.6 shows that the lattice parameters depended on the heat treatment. It can be seen that the c parameter is almost independent of the heat treating condition, however, the a and b lattice parameters increase with the
quenching temperature. Note that the levitated specimen has the largest a and b lattice parameters. In this specimen, because of the very fast cooling rate, no σ phase precipitated upon cooling. Hence, the composition of the β phase is expected to be similar to a sample quenched from above the β transus, i.e. above 1400°C. The fact that the ORTH1 phase was observed in the regions of the β matrix away from the σ grains in the 1300°C aged sample suggests that chemical composition of the β phase may play a role in the variation of the lattice parameters.

The habit plane of plates that possessed the ORTH1 phase was determined at the [001]_ortho || [011]_β orientation using the same method previously described for the HCP phase. The results consistently showed that the habit plane normal of these plates was 11° (±1°) from the (2T1)_β plane normal in the direction towards the (TT1)_β plane normal. Figure 6.9 shows the habit plane normal relative to the (2T1)_β plane normal for the plate.

6.2.1.3 Thin Plates with the ORTH Structure

The thin plates with thicknesses of \( \approx 500\text{Å} \) showed the ORTH structure, although, their diffraction pattern showed distinct differences from the ORTH1 structure. Depending on the diffraction patterns, the ORTH structures observed in the thin plates are categorized as either ORTH2 or ORTH3. The ORTH2 plates showed diffuse diffraction in the form of small streaks instead of distinct spots for some reflections in appropriate SAED patterns. The ORTH3 plates showed no diffraction for the same reflections. The ORTH2 plates had a thickness of \( \approx 100\text{Å} \) and were found in all of the heat treated and cast samples. The ORTH3 plates were very thin, with a thickness of \( \leq 100\text{Å} \) and were only observed in the two samples that were heat treated at 1300°C and 1500°C.
Table 6.6. Shows the lattice parameters of plates with the ORTH\textsubscript{1} structure, where $\phi_1$ is the angle between the $(0\bar{1}1)_{\beta}$ and $(020)_{\alpha_2}$ reflections.

<table>
<thead>
<tr>
<th>Sample Condition</th>
<th>Lattice parameters (Å)</th>
<th>$\phi_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a ($\pm$0.021)</td>
<td>b ($\pm$0.059)</td>
</tr>
<tr>
<td>Levitated</td>
<td>5.944</td>
<td>9.914</td>
</tr>
<tr>
<td>1500°C</td>
<td>5.922</td>
<td>9.836</td>
</tr>
<tr>
<td>1400°C</td>
<td>5.808</td>
<td>9.796</td>
</tr>
<tr>
<td>1300°C</td>
<td>5.774</td>
<td>9.956</td>
</tr>
</tbody>
</table>
Figure 6.13 shows a thin plate that has a thickness of ~0.020µm (200Å) and the diffraction characteristics of the ORTH2 phase. The SAED pattern observed in Figure 6.13b was obtained from the [011]β zone axis and shows the same plate orientation that was previously shown for the HCP (Figure 6.1) and ORTH1 (Figure 6.9) phases.

A magnified SAED pattern of Figure 6.13b is shown in Figure 6.14 in order to more easily see the diffuse diffraction of the ORTH2 phase. In this pattern, very faint spots, labelled as R1 and R2, were observed at positions that corresponded to the (020) and (200) reflections of the ORTH1 phase. However, those positions that corresponded to the (110) and (1T0) reflections of the ORTH1 phase, labelled as R3 and R4, showed short diffuse streaks for the ORTH2 phase. Thus, the entire pattern showed that it consisted of alternating rows of diffraction spots and diffuse streaks. The diffuse streaks varied in length, but were typically less than ~0.045/Å and were elongated in a direction slightly rotated from the (100)_p reflection. It was also observed in this pattern that the relative intensity of the R5 and R6 spots was greater than that of the R1 and R2 spots.

The measurements from the SAED pattern of Figure 6.13 were conducted with only the distinct diffraction spots. This included only the spots that are indexed in this pattern as R1, R2, and R3. The calculated d-spacings of these reflections were as follows:

\[
\begin{align*}
R1 &= 4.941 \pm 0.018\text{Å} \\
R2 &= 2.985 \pm 0.007\text{Å} \\
R3 &= 2.550 \pm 0.005\text{Å}.
\end{align*}
\]

The angle between the R1 and (01T)_p reflections was measured to be 4.67° (±0.20°). The pattern also showed the R3 spot to be rotated slightly from the \{11T\}_p reflection.
Figure 6.13. Shows a thin plate with the ORTH2 structure. (a) TEM micrograph; (b) SAED pattern showing the orientation relationship between the ORTH2 plate and the β phase at the [011]β zone axis.
Figure 6.14. Enlarged SAED pattern showing the diffuse streaks and diffraction spots observed for the ORTH2 plates. The diffraction pattern shows the \([011]_\beta\) zone axis for the \(\beta\) phase.
The habit plane of the plates with the ORTH2 phase was determined at the [001]_{c2} || [011]_p orientation using the same method described earlier. The results consistently showed that the habit plane normal of these plates was 11° (±2°) from the (211)_p plane normal in the direction towards the (111)_p plane normal. Figure 6.13a shows the habit plane normal relative to the (211)_p plane normal for the plate.

Figure 6.15 shows a very thin plate that was observed to have a thickness of ~0.011μm (110Å) and the diffraction characteristics of the ORTH4 phase. The SAED pattern observed in Figure 6.15b was obtained from the [011]_p zone axis.

A magnified SAED pattern of Figure 6.15b is shown in Figure 6.16 in order to better observe the diffuse diffraction of the ORTH4 phase. This pattern resembled that of the ORTH2 phase (Figure 6.13) except that there was no diffraction intensity observed for the positions that corresponded to diffuse streaks in the ORTH2 phase. In this pattern, very faint diffraction intensity was observed for spots, labelled as R1 and R2, which corresponded to the (020) and (200) reflections of the ORTH1 phase (Figures 6.9). However, no diffraction intensity was observed for those positions that corresponded to the (110) and (110) reflections of these phases. It was observed in this pattern that the relative intensity was greater for the R3, R4, and R5 spots than for the R1 and R2 spots.

The measurement of the SAED pattern shown in Figure 6.15 was conducted in a similar manner as was done for the previous ORTH2 phase. Following are the calculated d-spacings of three reflections which are shown in the pattern marked as R1, R2, and R3:

\[
\begin{align*}
R1 &= 4.997 \pm 0.018\text{Å} \\
R2 &= 2.925 \pm 0.007\text{Å} \\
R3 &= 2.518 \pm 0.005\text{Å}.
\end{align*}
\]
Figure 6.15. Shows a thin plate with the ORTH3 structure. (a) TEM micrograph; (b) SAED pattern showing the orientation relationship between the ORTH3 plate and the β phase at the [011]_β zone axis.
Figure 6.16. Enlarged SAED pattern showing the missing diffraction spots for the ORTH3 plates. The diffraction pattern shows the [011]_β zone axis for the β phase.
The angle between the R1 and \((01\overline{1})_p\) reflections was measured to be 5.33° (±0.20°).

The pattern also showed that the spot marked as R3 was again rotated slightly from the \(\{1\overline{1}\overline{1}\}_p\) reflection.

The habit plane of the plate shown in Figure 6.15a was determined at the \([001]_{02} \parallel [011]_p\) orientation using the same method described earlier. This analysis showed that the habit plane normal of this plate was 11° (±1°) from the \((2\overline{1}1)\beta\) plane normal in the direction towards the \((1\overline{1}\overline{1})\beta\) plane normal. The habit plane normal relative to the \((2\overline{1}1)\beta\) plane normal is shown for the plate in Figure 6.15a.

6.2.2 Plate Morphology

The determination of the plate morphology involved a comparison of the images of similar plates at three different orientations. Figure 6.17 shows plates at the following three orientations:

- \([001]_{ORTH} \parallel [0001]_{HCP}\) (Figure 6.17a)
- \([1\overline{1}0]_{ORTH} \parallel [1\overline{1}0\overline{0}]_{HCP}\) (Figure 6.17b)
- \([1\overline{1}0]_{ORTH} \parallel [1\overline{1}00]_{HCP}\) (Figure 6.17c).

At the orientations shown in Figures 6.17a and 6.17b, the plates have well defined interfaces with the B2 phase and high aspect ratios of length (l) to thickness (t), or (l/t). The interface is inclined relative to the beam direction for the plate shown in Figure 6.17b, but it is edge-on for the plate shown in Figure 6.17a. These observations are consistent with the sides of a plate shape since the angle between the \([001]_o\) and \([1\overline{1}0]_o\) directions is 90°, and this represents a rotation around a direction perpendicular to the plate face. The actual face of the plate was confirmed by choosing a third orientation, shown in Figure 6.17c, to show that the plate was oriented with its face normal close to the beam direction. In this figure, the plate does not have a well defined interface and its thickness was considerably larger than...
Figure 6.17. TEM micrographs showing the plate morphology that was determined from the images of plates at the three orthogonal directions. (a) the [001]₀ zone axis; (b) the [110]₀ zone axis; (continued)
Figure 6.17. (continued) (c) the [1\(\bar{1}0\)]_0 zone axis.
at the other two orientations. Thus, this observation was also consistent with a plate shape since the \([1\overline{1}0]_o\) direction lies 90° from the \([001]_o\) and ~60° from the \([110]_o\) directions.

Figure 6.18 shows a plate that was observed to be almost entirely enclosed within the thickness of the thin foil specimen. This orientation enabled a more complete assessment of the plate morphology. The dark and light contrast oscillations indicate that the thickness of the plate increases from its outer edges towards its center. There are several other plates observed in this figure that are oriented nearly edge-on within the specimen and have thin cross-sections.

6.2.3 Zig-Zag Plate Morphology

It was shown in chapter 4 that the microstructures of samples containing plates resembled a basket weave appearance. These microstructures were previously shown in Figure 4.8 for the levitated and drop quenched sample and in Figures 4.9a to 4.9c for the thermally aged and water quenched samples. Further analysis of these microstructures revealed that the basket weave appearance was due to plates that had formed with a zig-zag morphology from the \(\beta\) phase, as shown in Figure 6.19. These micrographs were obtained by orienting the sample in such a manner so as to show the two predominant variants of the zig-zag morphology. The general observations that were made from these BF and DF micrographs were that pairs of plates were always connected at an angle of ~60° to one another.

Figure 6.20 shows two plates that were connected to each other along a twin boundary and rotated ~60° from each other. The twin relationship between the two plates is demonstrated in the SAED pattern of Figure 6.20b. This pattern shows that
Figure 6.18. TEM micrograph showing plates that were partially enclosed within the thin foil specimen of the as-cast RAM sample of alloy 2.
Figure 6.19. TEM micrographs showing the zig-zag morphology of the plates. (a) bright field micrograph; (b) dark field micrograph.
both ORTH plates formed an orientation relationship with the \( \beta \) phase as follows:

\[
\begin{align*}
[110]_{p1} & \parallel [\overline{1}11]_{\beta} \quad \text{and} \quad (001)_{p1} \parallel (10\overline{1})_{\beta} \\
[110]_{p2} & \parallel [\overline{1}1\overline{1}]_{\beta} \quad \text{and} \quad (001)_{p2} \parallel (110)_{\beta}
\end{align*}
\]

(plate 1)

(plate 2).

For HCP plates, this relationship was as follows:

\[
\begin{align*}
[11\overline{2}0]_{p1} & \parallel [\overline{1}1\overline{1}]_{\beta} \quad \text{and} \quad (0001)_{p1} \parallel (10\overline{1})_{\beta} \\
[11\overline{2}0]_{p2} & \parallel [\overline{1}1\overline{1}]_{\beta} \quad \text{and} \quad (0001)_{p2} \parallel (110)_{\beta}
\end{align*}
\]

(plate 1)

(plate 2).

The diffraction pattern indicated that the \((2\overline{2}0)\) or \((2\overline{2}0)\) planes corresponded to the twin boundary, since these reflections were superimposed on the \((011)_{\beta}\) reflection of the \( \beta \) phase. The diffraction pattern also indicated that the \((001)_{\alpha}\) or \((0001)_{\alpha}\), planes of each of these twinned plates were aligned parallel to the \((\overline{1}0\overline{1})_{\beta}\) (plate 1) and the \((110)_{\beta}\) (plate 2) planes. Thus, the interplanar angle which separates the \(\{110\}_{\beta}\) planes accounts for the 60° angle and is a contributing factor in the development of the zig-zag morphology of the twinned plates.

6.2.4 Defect Structural Analysis of the Plates

The defect structures present in the ORTH and HCP plates consisted of planar faults, interfacial dislocations, and anti-phase domain boundaries (APDBs). In general, the thick HCP, medium thick ORTH1, and thin ORTH2 plates showed all of these defects. The thin ORTH3 plates did not appear to show any of these defects. However, these plates could not be identified at all of the different orientations that were necessary to conduct the complete defect analysis due to their thin size. The planar faults of the plates were always found to have the same crystallographic relationship with the \( \beta \) phase, irregardless of the plate phase. The interfacial dislocations were always observed for the HCP plates, only occasionally for the
Figure 6.20. Shows two plates connected together along a twin boundary. (a) TEM micrograph; (b) SAED pattern at the $[\overline{1}1\overline{1}]_p$ zone axis of the $\beta$ phase showing the twin relationship between plate 1 and plate 2.
ORTH1 plate, and never for the ORTH2 plates. The APDBs were distinctly different in the HCP plates as compared to the ORTH plates.

The planar faults were observed in the HCP, ORTH1, and ORTH2 plates. These faults were always observed in plates that were oriented edge-on at the [111] zone axis. From the orientation relationships observed for these plates, the edge-on orientation of the plates pertained to the [110] zone axis for the ORTH1 plate and the [1120] zone axis for the HCP plates. These faults were located parallel to the (001), or (0001) planes and were found to obey the invisibility criterion as shown in Figure 6.21. Figure 6.21a indicates the planar faults were invisible using the (002), or (0002) reflection, but were visible using the (211), or (2201) reflection as shown in Figure 6.21b. These results are consistent with stacking faults and indicate that they are running parallel to the (001), or (0001) planes.

Dislocations were observed at the interface between the plates and β matrix. The interfacial dislocations observed for the plate shown in Figure 6.21a appeared to be also associated with the stacking faults. However, it was found that the imaging conditions that made the stacking faults invisible did not always make the dislocations invisible as well. Unfortunately, the Burgers vector analysis of these interfacial dislocations was inconclusive. Nevertheless, these interfacial dislocations were believed to be misfit dislocations that formed during plate thickening.

The APDBs were observed in the HCP, ORTH1, and ORTH2 plates. The HCP plates showed APDBs that were different from the APDBs in the ORTH plates. This observation was based on a comparison of DF images using equivalent reflections for plates oriented edge-on at the [011] zone axis. These reflections were present in the SAED patterns of the [001] zone axis for the ORTH1 plate and the [0001] zone axis.
Figure 6.21. TEM micrographs showing the stacking faults observed in the plates at the [110]₀ or [1120]ₜ zone axes. (a) shows that the stacking faults were invisible using \( g = (002)₀ \) or \( (0002)_t \); (b) shows that the stacking faults were visible using \( g = (2\overline{1}1)_₀ \) or \( (2\overline{2}01)_t \).
for the HCP plates. Following are the equivalent reflections that were used to form the DF images:

\[ g = (12\overline{2}0)_H = (200)_O, \]

\[ g = (2\overline{1}10)_H = (1\overline{3}0)_O, \]

\[ g = (1\overline{1}20)_H = (130)_O. \]

Additional DF images were also obtained, as necessary, in order to determine the probable APDB vectors in the appropriate ORTH and HCP phases.

6.2.4.1 APDBs in HCP Plates

Typical APDBs that were observed in the HCP plates using reflections at the [0001]_H \parallel [011]_β zone axes are shown in Figure 6.22. The micrographs indicate that small domains formed in the plates and were visible in all three DF images. The DF image of Figure 6.22a was obtained using the (12\overline{2}0)_H and (100)_β reflections in order to show the APDBs of the HCP and B2 phases, respectively. There was some indication in this micrograph that the APDB of the B2 phase passed through the plate/β interface and into the plate. However, these APDBs were never observed to pass entirely across the plate, but instead curved into the plate and joined the smaller domain structure. It was also observed that the APDBs seen with the (12\overline{2}0)_H reflection were elongated in a direction parallel to the plate/β interface. The DF images of Figure 6.22b and 6.22c were formed with the (2\overline{1}10)_H and (1\overline{1}20)_H reflections, respectively, and showed a columnar morphology that extended from the mid-section of the plate outward to the plate/β interface. These columnar shaped APDBs extended in a normal direction from the midrib, which was not always well defined, to the interface.
Figure 6.22. TEM dark field micrographs showing the APDBs observed in the HCP plates. (a) \( g = (T\bar{2}10)_H \) and \( (100)_P \); (b) \( g = (\bar{2}110)_H \); (continued)
Figure 6.22. (continued) (c) $g = (11\overline{2}0)_H$. 

(c)

1000Å
Typical APDBs that were observed in the HCP plates also showed a columnar morphology when viewed at the $[\{11\overline{2}0\}]_H \parallel [\{1\overline{1}1\}]_p$ zone axes as shown in Figure 6.23. These APDBs were observed in DF images that were formed with the $(1\overline{1}00)_H$ and $(1\overline{1}01)_H$ reflections. Figure 6.23b shows the APDBs using the $(1\overline{1}01)_H$ reflection and indicates that the columnar APDBs in the plate were separated by a midrib. Figure 6.23a shows a BF image of the plate formed with the $(2200)_H$ reflection in order to show that the APDBs and midrib were invisible at this imaging condition.

The APDBs were found to exhibit an equiaxed morphology for plates oriented at the $[2\overline{1}10]_H$ zone axis as shown in Figure 6.24. The APDBs at this orientation were best observed using the DF imaging conditions of Figure 6.24b, which were formed using the $(01\overline{1}1)_H$ reflection. However, the APDBs still exhibited some residual contrast using the BF imaging conditions of Figure 6.24a, which was formed with the $(01\overline{1}0)_H$ reflection. In addition, stacking faults were also observed in these figures to be parallel to the $(0001)_H$ planes. However, the APDBs appeared to be unaffected by the stacking faults since they did not terminate at the faults.

6.2.4.2 APDBs in ORTH1 Plates

Typical APDBs that were observed in the ORTH1 plate using reflections at the $[00\overline{1}]_O \parallel [011]_p$ zone axes are shown in Figure 6.25. The DF image of Figure 6.25a was obtained with the $(200)_O$ and $(100)_p$ reflections in order to show the APDBs of the ORTH and B2 phases, respectively. This micrograph shows that the APDB observed in the B2 matrix maintained continuity upon passing through the plate/β interfaces of the plate. There were no other domains observed in the ORTH plates when imaged with the $(200)_O$ reflection. Therefore, the spacing between the segments of the coarse domains observed in the ORTH plates was comparable to the size of the APDBs.
Figure 6.23. TEM micrographs showing the columnar shaped APDBs observed in the HCP plates at the $[\bar{1}1\bar{2}0]_H \parallel [1\bar{1}1]_H$ zone axes. (a) bright field micrograph formed with $g = (2200)_H$; (b) dark field micrograph formed with $g = (1\bar{1}01)_H$. 
Figure 6.24. TEM micrographs showing the equiaxed morphology of the APDBs observed in the HCP plates at the $[2\overline{1}10]$$_h$ zone axis. (a) dark field micrograph formed with $g = (0\overline{1}10)_h$; (b) dark field micrograph formed with $g = (0\overline{1}11)_h$. 
observed in the B2 matrix. These coarse APDBs of the ORTH plates contrasted greatly with the APDBs observed in the HCP plates of Figure 6.21a, as both DF images were obtained at comparable reflections. The DF images obtained with the (130) and (130) reflections in Figures 6.25b and 6.25c, respectively, showed small APDBs with a columnar morphology that extended from a mid-rib near the center of the plate outward towards the plate/β interface. The appearance of the APDBs was similar in both DF images. The growth direction of these columnar shaped APDBs was ~31° from the interface normal which was nearly parallel to the (310) planes. The width of the domains was generally less than 200Å.

The fine APDBs observed in the ORTH plates also showed a columnar morphology when viewed at the [110] and [011] zone axes as shown in Figure 6.26. These fine APDBs were observed in DF images formed with (110) and (111) reflections. Figure 6.26 was obtained with the (111) reflection to show the APDBs and the midrib that separated the fine columnar APDBs in this plate.

The fine APDBs exhibited an equiaxed morphology for plates oriented at the [110] zone axis as shown in Figure 6.27. The DF micrograph in this figure was obtained with the (111) reflection. Stacking faults were also observed in Figure 6.27 to be parallel to the (001) planes. However, the fine APDBs appeared to be unaffected by the stacking faults since they did not terminate at the faults.

6.2.4.3 APDBs in ORTH2 Plates

The analysis of the APDBs of the ORTH2 plates showed that there were many similarities with the APDBs that were observed in the ORTH1 plates. Coarse APDBs were observed that passed through the interface from the B2 phase into the ORTH2 plates. Likewise, a high number density of very fine domains were also present in
Figure 6.25. TEM dark field micrographs showing the APDBs observed in the ORTH1 plates. (a) \( g = (200)_0 \) and \( (100)_p \); (b) \( g = (130)_0 \); (continued)
Figure 6.25. (continued) (c) \( g = (130)_c \).
Figure 6.26. TEM dark field micrograph showing the columnar shaped APDBs observed in the ORTH1 plates at the [110]₀ || [011]₀ zone axes using $g = (\overline{1}1\overline{1})_0$. 
Figure 6.27. TEM dark field micrograph showing the equiaxed morphology of the APDBs observed in the ORTH1 plates at the [1T0]_o zone axis using \( g = (111)_o \).
the ORTH2 plates and are shown in Figure 6.28. These fine domains were detected in DF images formed with the small diffuse streaks observed for those plates oriented at the [011]₀ zone axis, similar to Figure 6.15 for the ORTH2 structure. The position of this streak was near the (130)₀ reflection in reference to the ORTH1 plates. The domains were found to have a columnar morphology that extended from a midrib in the plate towards the interface in a direction normal to the streaks. The width of the domains was generally less than 100Å and the reciprocal length of the diffuse streaks in the SAED patterns was typically less than 0.04/Å.

In summary, the analysis of the APDBs indicated that the APDBs observed in the HCP plates were different from those observed in the ORTH1 and ORTH2 plates. The three different ORTH phases showed the same type of APDBs in these plates. The APDBs present in the HCP plates were not found to be dependent upon the different reflections that were used to form the DF images. This was opposite of that observed for the ORTH plates which showed both fine and coarse APDBs that depended on the specific DF imaging conditions. Table 6.7 lists all of the reflections that were used in the APDB study and the visibility/invisibility conditions observed for the APDBs in the HCP, ORTH1, and ORTH2 plates.

6.3 Discussion of the Plate Transformation

6.3.1 Martensitic Transformation

The results of this study suggest that the plates form from the β phase through a martensitic transformation. Rapid cooling rates obtained by water quenching and splat quenching resulted in the formation of plates. However, slower cooling rates were found to result in the formation of the ω-phase and the σ + γ
Figure 6.28. TEM dark field micrograph showing the columnar shaped APDBs observed in the thin ORTH2 plates using the diffuse streak. The specimen was tilted from the [011]_{\beta} zone axis of the \beta phase.
Table 6.7. The imaging conditions of the APDBs observed in the plates.

<table>
<thead>
<tr>
<th>Reciprocal Lattice g Vector</th>
<th>Plate Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HCP</td>
</tr>
<tr>
<td>{1120}_H</td>
<td>+</td>
</tr>
<tr>
<td>{1100}_H</td>
<td>+</td>
</tr>
<tr>
<td>{2200}_H</td>
<td>0</td>
</tr>
<tr>
<td>{1101}_H</td>
<td>+</td>
</tr>
<tr>
<td>{0002}_H</td>
<td>0</td>
</tr>
<tr>
<td>{2202}_H</td>
<td>0</td>
</tr>
<tr>
<td>(200)_O</td>
<td>----</td>
</tr>
<tr>
<td>(020)_O</td>
<td>----</td>
</tr>
<tr>
<td>(110)_O</td>
<td>----</td>
</tr>
<tr>
<td>(220)_O</td>
<td>----</td>
</tr>
<tr>
<td>(130)_O</td>
<td>----</td>
</tr>
<tr>
<td>(111)_O</td>
<td>----</td>
</tr>
<tr>
<td>(002)_O</td>
<td>----</td>
</tr>
</tbody>
</table>

The 0 means the APDBs were not observed. For the HCP phase, + means the APDBS were observed, but with no differences between them. For the ORTH phases, A pertains to the coarse APDBs while B pertains to the fine APDBs. The fine APDBs in the ORTH plates could possibly have obscured the detection of the coarse APDBs due to the small size and high number density.
microstructures. The lenticular-plate morphology and the associate habit plane are also consistent with the martensite morphology.

The following discussion describes the basic concept of the invariant line theory [94] so as to show the procedure for calculating the habit plane. The predicted habit plane is compared to those observed by TEM. The agreement between the calculated and observed habit planes confirm that the ORTH and HCP plates are formed from the β phase by a martensitic transformation.

The invariant line theory is consistent with the classical, or phenomenological, theory of martensitic transformations [79]. Both theories are based on a diffusionless transformation that involves the minimization of strain energy, which occurs from a shear-type lattice deformation. A lattice correspondence is first chosen between the parent and product phases. The habit plane is then calculated by applying to the lattice correspondence: a homogeneous strain that converts one Bravais lattice into another; an inhomogeneous strain that provides additional displacements, but causes no change in shape, to form the final structure; and a rigid body rotation that forms the invariant habit plane [79]. The strain energy from the martensitic transformation affects the kinetics and the morphology of the product phase. The product phase typically has a plate morphology and glissile interfaces that allow the composition, including atomic order, and lattice defects, such as APDBs, of the parent phase to be inherited by the product phase [95].

The classical theory and the invariant line theory both state that an invariant line exists in the habit plane [79,94]. The invariant line is a vector contained in both the parent and product phases that is unextended and unrotated by the martensitic transformation. Although both theories can be used to calculate the invariant line,
they will predict different values since the invariant line is treated differently in these theories. In the classical theory, the invariant line is considered a strain-free direction, while, in the invariant line theory it is considered a stress-free direction. The invariant line theory considers that a thin plate with principal strains of mixed signs are in a two-dimensional hydrostatic stress state, or plane stress condition [94]. The plate changes from a two-dimensional to a uniaxial stress state by rotating into a position that contains the uniaxial stress axis and the invariant line in the habit plane. The uniaxial stress axis is normal to the invariant line in the habit plane and is the axis that the rigid body rotation occurs around. This condition requires that two of the three principal strains, ε₁ and -ε₂, must have opposite signs and that the third one, ε₃, is nearly equal to zero [94]. If this condition is met, then the elastic strain ε₃ that is present in the direction of the uniaxial stress axis causes a Poisson contraction that is superimposed on the two other principal strains by an amount equal to νε₃. Thus, the calculated position of the invariant line using the invariant line theory will be modified from that using the classical theory when the Poisson contraction on these two principal strains are also considered.

The procedure that was used in this study for calculating the invariant line of the ORTH and HCP plates is covered in the following discussion. This procedure is based on the invariant line theory and is described for the ORTH1 plate observed in the 1400°C aged sample shown in Figure 6.9 and for the HCP plate observed in the 1300°C aged sample shown in Figure 6.1. The calculations were done using the specific lattice parameters of the ORTH1 and HCP plates observed in these figures. This was necessary since the calculations showed that the habit plane was sensitive to the lattice parameters of the β phase and the different phases of the plates. In
order to test the accuracy of the invariant line theory, the habit plane measured for
the ORTH1 plate in Figure 6.9 and the HCP plate in Figure 6.1 had to be compared to
the habit plane that was calculated using this theory.

The first step in the procedure for calculating the habit plane of the ORTH1
and HCP plates was to calculate the homogeneous distortion ($B$) from the principal
axes of strain ($\lambda$) that formed during the martensitic transformations of these plates.
There are three principal axes of strain, which are the eigenvalues of the linear
transformations that define three orthogonal directions in the parent $\beta$ phase that
transform into three orthogonal directions in the product phase [79]. These
orthogonal directions also undergo a rigid body rotation ($R$) as part of the martensitic
transformation, but this rotation does not cause any dimensional changes to these
directions. The homogeneous distortion ($B$) is described by a $3 \times 3$ matrix with the
three principal axes of strain as follows:

$$B = \begin{bmatrix}
\lambda_1 & 0 & 0 \\
0 & \lambda_2 & 0 \\
0 & 0 & \lambda_3
\end{bmatrix} = \begin{bmatrix}
\varepsilon_1 & 0 & 0 \\
0 & \varepsilon_2 & 0 \\
0 & 0 & \varepsilon_3
\end{bmatrix} + \begin{bmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{bmatrix}$$

where the matrix to the left of the equal sign shows the principal axes of strain, or
eigenvalues, while the first matrix following the equal sign shows the principal
strains and the last matrix is an identity matrix. The subscripts 1, 2 and 3 represent
directions along the $[100]_p$, $[0\bar{1}1]_p$, and $[011]_p$ axes, respectively, of the $\beta$ phase. By
definition, the principal strains of the homogeneous transformation are determined
from the eigenvalues by the relationship $\varepsilon_i = \lambda_i - 1$, where $i$ defines each of the three
orthogonal axes [79].
The principal axes of strain were calculated from the lattice parameters and the lattice correspondences between the β phase and each of the ORTH1 and HCP phases. The lattice correspondences were first determined from the orientation relationships as follows for the ORTH1 phase (Figure 6.9):

\[
\begin{align*}
[100]_β & \parallel [100]_O \\
[0\bar{T}1]_β & \parallel [010]_O \\
[011]_β & \parallel [001]_O
\end{align*}
\]

and for the HCP phase (Figure 6.1):

\[
\begin{align*}
[100]_β & \parallel [11\bar{2}0]_H \\
[0\bar{T}1]_β & \parallel [\bar{T}100]_H \\
[011]_β & \parallel [0001]_H
\end{align*}
\]

The principal axes of strain were then calculated from the lattice correspondences with the lattice parameters of the β, ORTH1, and HCP phases. Thus, following are the matrices of the homogeneous distortions determined from these calculations for the ORTH1 phase:

\[
\mathbf{B} = \begin{bmatrix}
2a_β/a_O & 0 & 0 \\
0 & 2\sqrt{2}a_β/b_O & 0 \\
0 & 0 & \sqrt{2}a_β/c_O
\end{bmatrix} = \begin{bmatrix}
1.083 & 0 & 0 \\
0 & 0.927 & 0 \\
0 & 0 & 0.994
\end{bmatrix}
\]

for the HCP phase:

\[
\mathbf{B} = \begin{bmatrix}
2a_β/a_H & 0 & 0 \\
0 & \sqrt{2}a_β/a_H \cos(30°) & 0 \\
0 & 0 & \sqrt{2}a_β/c_H
\end{bmatrix} = \begin{bmatrix}
1.119 & 0 & 0 \\
0 & 0.914 & 0 \\
0 & 0 & 0.996
\end{bmatrix}
\]

From the definition of the principal strains, it was found that the magnitudes of \(\varepsilon_1\)
and \( \varepsilon_2 \) were the largest, but of opposite signs, and that \( \varepsilon_3 \) was the closest to zero in the homogeneous distortions of the ORTH1 and HCP plates. This result indicated that the uniaxial stress axis for each of these different plates was parallel to the \([011]_\beta\) direction of the \( \beta \) phase. Therefore, the \([001]_o\) direction of the ORTH1 and the \([0001]_h\) direction of the HCP plates were the uniaxial stress axes that these plates rotated around to form the habit plane with the \( \beta \) phase. These directions were also confirmed by the calculations that showed that both \( \varepsilon_2 \) and \( \varepsilon_3 \) had negative values, but that the value of \( \varepsilon_3 \) was an order of magnitude less than the value for \( \varepsilon_2 \). Therefore, according to the invariant line theory, this condition indicated that the plate was uniaxially stressed along the smaller of the two similar strain values which was \( \varepsilon_3 \).

The next procedure in the invariant line theory was to add the effect of the elastic strain along the uniaxial stress axis to the homogeneous distortions of the ORTH1 and HCP plates. Since the invariant line in the habit plane is stress free according to this theory, then the elastic strain in the uniaxial stress axis causes an extension of \(-\varepsilon_3\) in this direction. This extension then causes a Poisson contraction by an amount of \(\nu\varepsilon_3\) on the other two principal strains. Thus, following is the additional effect of this extension on the principal axes of strain in the homogeneous distortion (\( B \)):

\[
B' = \begin{bmatrix}
\lambda_1 & 0 & 0 \\
0 & \lambda_2 & 0 \\
0 & 0 & \lambda_3
\end{bmatrix} + \begin{bmatrix}
\nu \varepsilon_3 & 0 & 0 \\
0 & \nu \varepsilon_3 & 0 \\
0 & 0 & -\varepsilon_3
\end{bmatrix} = \begin{bmatrix}
\lambda_1' & 0 & 0 \\
0 & \lambda_2' & 0 \\
0 & 0 & \lambda_3'
\end{bmatrix}
\]

where \( \nu \) is the Poisson ratio and is assumed to be 0.3. The effect of the modified homogeneous distortion \( B' \) is to minimize the elastic strain energy of the plates and to leave them in an orientation containing the habit plane. The schematic in Figure
6.29 shows the plate in this uniaxially stressed state and the three principal axes of strain. The habit plane of the plate shown in this figure contains both the uniaxial stress axis along $\lambda_3$, which is the direction that the plate rotated around, and the invariant line which is normal to the uniaxial stress axis and is unextended.

The final procedure is to calculate the invariant line in the habit plane of the ORTH1 and HCP plates using the modified homogeneous distortion $B'$ and the rigid body rotation $R$. These calculations were done following the method described in the classical theory of martensitic transformations [79]. From this theory, the total transformation $T$ of the ORTH1 and HCP plates in matrix notation is as follows:

$$
T = B'R = \begin{bmatrix}
\lambda'_1 & 0 & 0 \\
0 & \lambda'_2 & 0 \\
0 & 0 & \lambda'_3
\end{bmatrix}
\begin{bmatrix}
\cos \theta & \sin \theta & 0 \\
- \sin \theta & \cos \theta & 0 \\
0 & 0 & 1
\end{bmatrix}
$$

The rotation axis in $R$ is the $[011]_\beta$ direction of the $\beta$ phase, which is parallel to the $[001]_{\text{orth}}$ direction of the ORTH1 plate and the $[0001]_{\text{HCP}}$ direction of the HCP plate. These directions define the uniaxial stress axis of the transformation $T$. A vector $u$ will be the invariant line in the habit plane of the plates when the following is true:

$$
Tu = u,
$$

which indicates that $u$ is undistorted by the transformation $T$. The invariant line $u$ was calculated from the eigenvalues $\lambda$ of the transformation $T$ and is described by the matrix equation:

$$
Tu = \lambda u, \text{ or }
|T - \lambda I|u = 0.
$$

The non-trivial solutions of this equation were then determined by setting the
Figure 6.29. Shows the uniaxial stress state of the plate and the three principal axes of strain which are $\lambda_1$, $\lambda_2$, and $\lambda_3$. 
determinant of the equation to zero:

\[ \det |T - \lambda I| = 0, \]

which has the three eigenvalues \( \lambda_1, \lambda_2, \) and \( \lambda_3. \) Since the invariant line is unrotated and undistorted, then the vector \( \mathbf{u} \) was found by setting one of the eigenvalues to unity and solving the determinant. The rigid body rotation \( \phi \) between the \( \beta \) phase and the ORTH1 and HCP phases is solved from the previous equation for \( \lambda = 1 \) and is as follows:

\[ \cos \phi = \frac{1 + \lambda_1 \lambda_2}{\lambda_1 + \lambda_2}. \]

This rotation brings the undistorted vectors in the \( \beta \) phase and the ORTH1 or HCP phases into coincidence with one another to form the invariant line \( \mathbf{u} \) in the habit plane of these plates.

The calculations for the ORTH1 plate shown in Figure 6.9 indicated that the invariant line is 42.71° (± 0.23°) from the (100)\(_{\beta}\) plane. Converting this angle from the ORTH1 phase to the \( \beta \) phase showed that this line is 47.15° (± 0.23°) from the (100)\(_{\beta}\) plane. The difference between these two angles is equal to the rigid body rotation \( \phi \), which is 4.44° (± 0.23°). These calculations showed good agreement with the habit plane and rigid body rotation observed for the ORTH1 plate in Figure 6.9.

The habit plane of this plate was measured as 12.41° (± 0.08°) from the (2\( \overline{T} \)1)\(_{\beta}\) plane or 47.67° (± 0.08°) from the (100)\(_{\beta}\) plane, since the angle between the (2\( \overline{T} \)1)\(_{\beta}\) and (100)\(_{\beta}\) planes is 35.26°. Therefore, the calculated angle for the invariant line of the habit plane is only ~0.5° from the measured angle for the habit plane of this ORTH1 plate. The rigid body rotation was determined from the orientation relationship shown in the SAED pattern of Figure 6.9 by measuring the angle between the (010)\(_{\beta}\) plane of
the ORTH1 phase and the (0T1)β plane of the β phase. The measured angle was 4.67° (± 0.08°), which is 0.23° larger than the calculated angle of the rigid body rotation.

The HCP plate shown in Figure 6.1 was also found to show good agreement between the calculated and the experimentally measured habit plane. The calculations showed that the invariant line in the habit plane is 39.27° (± 0.23°) from the (1T00)H plane of this HCP plate, which is also 45.05° (± 0.23°) from the (100)β plane of the β phase. The difference between the two angles of the HCP and β phases is equal to the rigid body rotation, which was calculated to be 5.78° (± 0.23°). The comparison of the calculated angle to the measured angle of the habit plane shows that these two angles are different from one another by only 0.13°. This result was determined from the measurements that showed that the habit plane of the HCP plate shown in Figure 6.1 was 44.92° (± 0.08°) from the (100)β plane. Likewise, there is good agreement between the calculated and the measured angles of the rigid body rotation. From the SAED pattern of the orientation relationship shown in Figure 6.1, the measured angle between the (100)β and (1T00)H reflections was 5.58° (± 0.08°), which is 0.20° less than the calculated angle.

In summary, it was shown in this discussion that the invariant line theory is able to accurately predict the invariant line in the habit plane of the ORTH1 and HCP plates. The specific lattice parameters and the habit plane measured for the ORTH1 and HCP plates had to be used so that the ability of this theory to predict the habit plane could be tested. It was found in this study that when the specific values of the lattice parameters were used for a particular ORTH1, ORTH2, or HCP plate, then the calculations based on the invariant line consistently showed good agreement with the measured habit plane of these plates. The agreement between the
calculated angles and the measured angles was within acceptable ranges based on the measurement errors associated with the TEM. Thus, it is concluded that the ORTH and HCP plates formed from the β phase by a martensitic transformation based on the results of this study.

6.3.2 Structural Analysis of the Plates

The structural analysis of the ORTH1 and HCP plates using SAED and CBED techniques showed them to be closely related to each other. This was observed in the orientation relationships with the β phase and in the interplanar d-spacings and angles measured from reflections in SAED patterns.

The schematic in Figure 6.30 shows the relationship between the ORTH1 and HCP phases. The unit cells of these phases are superimposed upon each other to illustrate how the distortions of the orthorhombic phase are related to the hexagonal phase. The dotted lines outline the ORTH1 unit cell with the ao and bo lattice parameters normal to the [001]o direction. The HCP unit cell is shown normal to the [0001]H direction. The HCP unit cell is shown with both the usual hexagonal representation using the ah lattice parameter, and also with the orthorhombic representation using the aH,o and bH,o lattice parameters. The hexagonal structure requires that the two ah axes be separated by 120°. This makes the a/b ratio a constant of √3 or 0.577. From this schematic, it can be seen that distortions in the aH,o and bH,o directions can destroy the hexagonal structure and form the orthorhombic structure with an a/b ratio that would normally not be equal to 0.577. The a/b ratios of the ORTH1 structure determined from Table 6.6 are ~0.580 to 0.602, which are larger than 0.577. These values are obtained by a decrease in the aH,o
Figure 6.30. Shows the unit cells of the ORTH1 and HCP phases superimposed upon each other to illustrate how the distortions of the orthorhombic phase are related to the hexagonal phase. The drawing shows the [001]_O direction of the ORTH1 unit cell and the [0001]_H direction of the HCP unit cell.
lattice parameter and an increase in the $b_{\text{HCP}}$ lattice parameter which are due to the orthorhombic distortions.

A difference in the atomic site occupancy is suggested to be responsible for the distortions of the HCP phase to an orthorhombic phase. However, before discussing the atomic site occupancy of the ORTH1 and HCP phases, it is important to discuss the APDBs that were present in these phases and the effect that the $\beta$ composition had on them. Information obtained in each of these two following sections will be used in the two sections that deal with the atomic site occupancy of the ORTH1 and HCP phases.

6.3.2.1 The APDBs

The presence of APDBs in the plates indicated that disorder to order transitions had occurred in the plates as they developed. Thus, the presence of different types of APDBs implied that the HCP and ORTH1 plates followed different structural development paths. The most apparent differences in the APDBs were observed in the DF images of the HCP plate (Figures 6.22a) and the ORTH1 plate (Figure 6.25a) that were formed with the $(12\overline{1}0)_\text{H}$ and $(200)_\text{O}$ reflections, respectively. By incorporating the $(100)_\beta$ reflection along with each of these reflections in the SAED aperture; the APDBs present in the B2 matrix, the numerous small APDBs in the HCP plates, and the few coarse APDBs in the ORTH1 plates were simultaneously observed. This technique showed that the APDBs in the B2 matrix were connected to the coarse APDBs in the ORTH1 plates, which were often observed to pass across the plates. This observation was not made for the APDBs present in the HCP plates.

There were additional differences that were observed in the APDBs present in the HCP and ORTH1 plates when other reflections were used to form the DF images.
The coarse APDBs in the ORTH1 plates were not observed when the (130)_o and (130)_0 reflections were used, but instead a high number density of small APDBs were observed (compare Figure 6.25a to Figures 6.25b and 6.25c). This result was different for the APDBs present in the HCP plates which showed the same general appearance in all three imaging conditions (compare Figure 6.22a to Figures 6.22b and 6.22c). Even though a columnar morphology was observed for the APDBs in the HCP plates and for the fine APDBs in the ORTH1 plates, the scale and the orientation of these columnar APDBs were different. The results indicated that the columnar APDBs in the HCP plates were oriented normal to the habit plane, while the fine APDBs in the ORTH1 plates were oriented by up to ~30° from the habit normal. However, the columnar APDBs were observed normal to the plate interface for the HCP plates at the [1120]_H zone axis and for the ORTH1 plates at the [110]_o zone axis. Therefore, the [1120]_H and [110]_o zone axes showed the APDBs in the HCP and ORTH1 plates, respectively, at an orientation that was 90° from the [001]_H and [001]_o zone axes. The analysis of the plates indicated these two orientations represented a 90° rotation about the habit normal of the HCP and ORTH1 plates. Thus, the vector representing the ~30° angle between the habit normal and the direction of the columnar APDBs in the ORTH1 plates was parallel to the electron beam at the [110]_o zone axis. This explains why these APDBs were observed normal to the interface of the ORTH1 plates at this orientation.

The displacement vector of the APDBs was important to determine, since it will be used later in the discussion to show the atomic site occupancy of the ORTH1 and HCP phases. The displacement vector was calculated for possible vectors from the literature using the imaging principles of α-boundaries [96]. These boundaries, or
interfaces, impart a phase shift described by the formula \( \alpha = 2\pi(g \cdot R) \) on the normal scattering phase \( \phi = 2\pi(g \cdot s) \) where \( R \) is the displacement vector associated with the APDB, \( s \) is the deviation parameter, and \( g \) is the reflection vector. The APDBs will be invisible when \( (g \cdot R) = n\pi \), where \( n \) is an even integer, since they will then have the same phase as the normal scattering phase. Likewise, the APDBs will be visible when \( n \) is an odd integer, or out of phase with the normal scattering phase. Thus, these visible/invisible imaging characteristics of the APDBs are responsible for the imaging conditions shown in Table 6.7.

The most probable displacement vector, out of all of the possible vectors, for the APDBs in the HCP plates was \( 1/6<11\overline{2}0> \). Previous studies had shown that this vector was associated with the ordering reaction of the \( \alpha \)-Ti phase to the \( \alpha_2\)-Ti\(_{3}\)Al phase [78]. The calculated phase factors using \( \alpha = 2\pi(g \cdot R) \) for this displacement vector and for several \( g \) reflections are shown in Table 6.8. A Comparison of these calculated values in this table to the observed imaging conditions in Table 6.7 shows good agreement between the visible and invisible conditions. Thus, the \( 1/6<11\overline{2}0> \) displacement vector is descriptive of the APDBs in the HCP phase.

Analysis of the APDBs in the ORTH1 and ORTH2 plates revealed that the displacement vector for the fine APDBs is \( 1/2[100] \), while the displacement vector for the coarse APDBs is \( 1/4[110] \). Table 6.9 lists the calculated phase factors of these APDB vectors for several \( g \) reflection vectors. Comparing the calculated values in Table 6.9 to the observed imaging conditions in Table 6.7 showed that \( 1/2[100] \) is the correct vector for the fine APDBs and that \( 1/4[110] \) is the vector for the coarse APDBs in these ORTH1 and ORTH2 plates. These two specific displacement vectors for the
Table 6.8. Calculated phase factors, $\alpha = 2\pi(g \cdot R)$, for the APDB vectors in the HCP phase.

<table>
<thead>
<tr>
<th>Reflection g Vector</th>
<th>APDB Vectors</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1/6[1120]</td>
</tr>
<tr>
<td>(1120)</td>
<td>0</td>
</tr>
<tr>
<td>(1210)</td>
<td>-$\pi$</td>
</tr>
<tr>
<td>(2110)</td>
<td>-$\pi$</td>
</tr>
<tr>
<td>(1000)</td>
<td>0</td>
</tr>
<tr>
<td>(1010)</td>
<td>$\pi$</td>
</tr>
<tr>
<td>(0110)</td>
<td>$\pi$</td>
</tr>
<tr>
<td>(1101)</td>
<td>0</td>
</tr>
<tr>
<td>(1011)</td>
<td>$\pi$</td>
</tr>
<tr>
<td>(0111)</td>
<td>$\pi$</td>
</tr>
<tr>
<td>(2200)</td>
<td>0</td>
</tr>
<tr>
<td>(2020)</td>
<td>0</td>
</tr>
<tr>
<td>(0220)</td>
<td>0</td>
</tr>
<tr>
<td>(0002)</td>
<td>0</td>
</tr>
</tbody>
</table>
Table 6.9. Calculated phase factors, $\alpha = 2\pi(g \cdot \mathbf{R})$, for the APDB vectors in the ORTH1 and ORTH2 phases.

<table>
<thead>
<tr>
<th>Reflection g Vector</th>
<th>APDB Vectors</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1/2[100]</td>
</tr>
<tr>
<td>(200)</td>
<td>0</td>
</tr>
<tr>
<td>(020)</td>
<td>0</td>
</tr>
<tr>
<td>(002)</td>
<td>0</td>
</tr>
<tr>
<td>(110)</td>
<td>$\pi$</td>
</tr>
<tr>
<td>(220)</td>
<td>0</td>
</tr>
<tr>
<td>(130)</td>
<td>$\pi$</td>
</tr>
<tr>
<td>(260)</td>
<td>0</td>
</tr>
<tr>
<td>(111)</td>
<td>$\pi$</td>
</tr>
</tbody>
</table>
fine and coarse APDBs correlate with results previously published in the literature for the O-Ti$_2$AlNb phase [31,34].

### 6.3.2.2 Effect of the β Composition

Assuming that the plates have formed by a martensitic reaction, then they must have inherited the composition of the β matrix. From chapter 4, it was found that the microstructures of the aged samples consisted of the single β phase at temperatures of ≥1400°C and the σ + β phases at 1300°C. The composition values shown in Table 4.1 indicated that the composition of the β matrix at 1400°C was increased by 3%Ti (to 37%Ti) and decreased by ~4%Nb (to 23%Nb) upon formation of the σ grains at 1300°C. The Al content in the β matrix was observed to stay nearly constant between 1400°C and 1300°C. This composition change explains the change in lattice parameters observed upon a variation in quenching temperature. Results by Kestner-Weykamp et al. [26] showed a similar dependency on the composition of the β phase, in which a change in the composition of the β phase from 20Nb to 30Nb (at.%) in Ti-25Al-XNb (at.%) based alloys increased the a/b ratio of the O-Ti$_2$AlNb phase from 0.632 to 0.645.

There were two ways that the β composition may have affected the structure of the plates: one is related to the content of the Al and the other to the content of the Ti. The primary effect of the Al content is to lower the magnitude of the orthorhombic distortion. This effect is determined by comparing the a/b ratios of the ORTH1 plates, which were 0.580 and ≤0.602, to the equilibrium O-Ti$_2$AlNb phase which was >0.630 [28]. The lower a/b values were attributed to the higher Al content, which is ~40Al (at.%) in alloy 2 as compared to ~25Al (at.%) in the stoichiometric composition of the O-Ti$_2$AlNb phase. This comparison shows that Al must have
substituted for Ti since the ~27Nb (at.%) content of alloy 2 was essentially the same
as that in the O-Ti$_2$AlNb phase. The lowering of the a/b ratio by an increase in the Al
content is the opposite of what has been observed in previous work by an increase in
the Nb content [26]. Thus, it is deduced from this study that the Al content must
have reduced the orthorhombic distortions, which causes the a/b ratio to approach the
a/b ratio of the HCP phase in alloy 2. If the Ti content of the β matrix were also high,
in addition to the ~40%Al content, then together they might have stabilized the HCP
phase in the plates. Therefore, the effect of Ti is to act with Al to stabilize the HCP
phase, instead of the ORTH phase in the 1300°C aged sample of alloy 2.

6.3.2.3 Atomic Site Occupancy

6.3.2.3.1 The ORTH1 and ORTH2 Phases

It is asserted from this study that the ORTH1 phase is related to the
α'' martensite and the O-Ti$_2$AlNb phase, except that the atomic site occupancy of the
ORTH1 phase is modified by the greater amount of Al content in alloy 2. There were
many similarities between the ORTH1 plates that formed in alloy 2, the α''
martensite that formed in Ti-Nb alloys [62], and the O-Ti$_2$AlNb phase that formed in
the Ti$_3$Al + Nb alloys [13]. The ORTH1 plates form by a martensitic transformation
similar to the α'' martensite, but the ORTH1 plates are structurally similar to the
O-Ti$_2$AlNb phase based on the lattice parameters, orientation relationship with the β
phase, base-centered orthorhombic Bravais lattice with mmm point group, and
APDBs. It will be shown in this section that all three phases are structurally linked
through the same Cmcm space group. The structural difference between these
phases depends primarily on whether these phases have the disordered Cmcm
structure (α'' martensite) or the ordered Cmcm structure (O-Ti$_2$AlNb phase and
ORTH1 plates). Unfortunately, direct proof of the structural relationship between the ORTH1 phase and the O-Ti₂AlNb phase was unobtainable, since the CBED analysis of the ORTH1 plates was complicated by the small thicknesses and internal defects. Internal defects such as stacking faults and APDBs are lattice imperfections that destroy the conclusive evidence of glide-plane and screw-axis symmetry elements in CBED patterns [89].

Indirect proof of the structural relationship between the ORTH1 phase and the O-Ti₂AlNb phase is established by the determination of a similar ordered Cmcm space group for the ORTH1 phase. Determination of the ordered Cmcm space group for the ORTH1 phase is based on the orientation relationship; mmm point group symmetry; absent (100), (010), and (001) reflections; and APDBs. The results of this study established that the ORTH1 phase has the mmm point group symmetry by showing a 2mm symmetry for the [001] and [110] zone axes and a mirror plane parallel to the (001) planes. The SAED patterns of the [001] zone axis showed that the (100) and (010) reflections were forbidden and that the (110) reflection was allowed. These were consistent with the structure factor of a base-centered Bravais lattice, i.e. \((h + k) = n\), where odd \(n\) is forbidden and even \(n\) is allowed. Finally, the APDBs that were observed in the ORTH1 plates showed indirect proof that the ORTH1 phase had the Cmcm space group. This proof was based on the APDB analysis that showed that the displacement vector for the fine columnar APDBs was 1/2[100] and for the coarse APDBs was 1/4[110]. These two specific displacement vectors in the ORTH1 phase are the same as those observed in the O-Ti₂AlNb phase [31,34], which suggests that the three separate sublattices in the ORTH1 phase are similar to those in the O-Ti₂AlNb phase. These sublattices could have different
atomic arrangements, but still show the necessary \(2_1\) screw-axis and c-glide plane of the Cmcm space group. Thus, all of these observations are consistent with the Cmcm space group and indicate that the ORTH1 phase has a similar space group to the O-Ti\(_2\)AlNb phase.

The proposed atomic site occupancy of the ORTH1 phase is based on the three sublattices and the higher Al content of alloy 2, compared to that in the O-Ti\(_2\)AlNb phase. This proposed model is shown in Figure 6.31. The difference between this model and the O-Ti\(_2\)AlNb phase is that the Ti and Al positions are exchanged between the 8g and 4c1 sites with the Al occupying the 8g, Ti the 4c1, and Nb the 4c2 Wyckoff sites. The atomic site occupancy of the ORTH1 phase is listed in Table 6.10. In this model, the unit cell of the ORTH1 phase consists of alternating rows of Ti-Nb and Al-Al bonds in the [100] directions, and alternating rows of Ti-Al and Nb-Al bonds in the [110] directions. The strong bonds between Ti-Al and Nb-Al act as rigid chains in the lattice along the [110] direction. These chains then keep the weak bonds between Ti-Nb strictly in the [100] direction. This suggests that the orthorhombic distortions in the ORTH1 phase are due to the Ti-Nb and Al-Al bonds in the [100] directions. Thus, the coordinates of the atoms listed in Table 6.10 and shown in Figure 6.31 are assumed to be (0, 0.1667, 0.25) for Ti on the 4c1 site; (0, -0.1667, 0.25) for Nb on the 4c2 site; and (0.25, 0.0833, 0.25) for Al on the 8g site.

This model for the site occupancy of the ORTH1 phase is derived from the O-Ti\(_2\)AlNb phase by considering that Al substitutes for Ti. Therefore, an increase in the Al composition of the O-Ti\(_2\)AlNb phase, with constant Nb, must be accomplished by occupying either the 8g sites with Ti or the 4c2 sites with Nb. The most likely scenario would be for the Al to occupy the 4c2 sites. This maximizes the number of
Table 6.10. The proposed atomic site occupancy of the ORTH1 phase with the $\text{Al}_2\text{NbTi}$ stoichiometry and the Cmcm (63) space group.

<table>
<thead>
<tr>
<th>Site Number</th>
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<th>Element</th>
<th>Wyckoff Position</th>
</tr>
</thead>
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</tr>
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<td>0.25</td>
</tr>
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<td>0.25</td>
</tr>
<tr>
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<td>0.4167</td>
<td>0.25</td>
</tr>
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<td>0.9167</td>
<td>0.25</td>
</tr>
<tr>
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<td>0.0833</td>
<td>0.75</td>
</tr>
<tr>
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<td>0.5833</td>
<td>0.75</td>
</tr>
<tr>
<td>7</td>
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<td>0.0833</td>
<td>0.75</td>
</tr>
<tr>
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<td>0.75</td>
<td>0.5833</td>
<td>0.75</td>
</tr>
<tr>
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<td>0.25</td>
</tr>
<tr>
<td>10</td>
<td>0.5</td>
<td>0.1667</td>
<td>0.25</td>
</tr>
<tr>
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<td>0.3733</td>
<td>0.75</td>
</tr>
<tr>
<td>12</td>
<td>0.5</td>
<td>0.8333</td>
<td>0.75</td>
</tr>
<tr>
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<td>0.1667</td>
<td>0.25</td>
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<tr>
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<td>0.8333</td>
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</tr>
<tr>
<td>16</td>
<td>0.5</td>
<td>0.3733</td>
<td>0.75</td>
</tr>
</tbody>
</table>

The following Wyckoff values were used:
- $\text{Al} (8g)$ \((x, y, z) = (0.25, 0.0833, 0.25)\)
- $\text{Ti} (4c_1)$ \((x, y, z) = (0, 0.1667, 0.25)\)
- $\text{Nb} (4c_2)$ \((x, y, z) = (0, -0.3333, 0.25)\).
Figure 6.31. Shows the proposed atomic site occupancy of the ORTH1 phase based on the Cmcm space group with Al atoms occupying the 8g, Ti atoms occupying the 4c1, and Nb atoms occupying the 4c2 Wyckoff positions.
Ti-Al bonds which have the strongest bonds and the shortest bond length [84]. When a sufficient number of 4c2 sites are filled by Al and in addition to the 4c1 sites already occupied by Al, then these form the basis of the 8g sites in the proposed ORTH1 phase. As a consequence of the increase in Al and subsequent occupancy of the 8g sites, the Ti is forced to occupy the 4c1 sites and Nb is reassigned to the 4c2 sites in the new ORTH1 phase.

Evidence that Al occupies the 8g Wyckoff sites in the proposed ORTH1 phase is obtained in this study by comparing the relative intensities of the (020)₀ and (110)₀ reflections with the calculated structure factors. The intensity of these reflections were shown in the CBED pattern of Figure 6.11. The structure factors of the (020)₀, (110)₀, and other reflections at the [001] orientation were then calculated based on the atomic occupancies of the ORTH1 and O-Ti₂AlNb phases. Figure 6.32 shows the relative intensities of these two phases in the form of calculated CBED patterns for comparison with the actual CBED pattern in Figure 6.11. The calculated patterns showed the best match between the ORTH phase (Figure 6.32a) and the CBED patterns of the ORTH1 plates (Figures 6.11), since both patterns indicated that the intensity of the (020) reflection was greater than the (110) reflection. The opposite was true of the O-Ti₂AlNb phase (Figure 6.32b) which showed that the intensity of the (110) reflection was greater than the (020) reflection. Thus, this comparison shows that Al, and not Ti, must occupy the 8g sites in the ORTH1 phases.

Further proof of the proposed site occupancy for the ORTH1 phase in alloy 2 was obtained by conducting the CBED analysis on plates that were present in a Ti-rich alloy (designated as alloy 1). The composition of alloy 1 was 40Ti-32Nb-28Al (at.%). This composition is close to the 45Ti-30Nb-25Al (at.%) composition of an alloy
Figure 6.32. Shows the calculated CBED patterns of the orthorhombic structures based on two possible atomic site occupancies. (a) the proposed ORTH1 phase with the stoichiometry of Al$_2$TiNb; (b) the O-Ti$_2$AlNb phase [13].
that contained a single O-Ti$_2$AlNb phase microstructure after aging at 800°C [26]. Therefore, alloy 1 was heat treated at 1400°C for 4 hours to form the single β phase and then furnace cooled, which resulted in the formation of a high number density of O-Ti$_2$AlNb plates from the B2 matrix. The structure of the O-Ti$_2$AlNb plates was confirmed by the SAED and CBED analysis. The SAED analysis showed that the orientation relationship between the O-Ti$_2$AlNb and B2 phases was [001]$_o$ ||[011]$_p$ zone axes with the (110)$_o$ planes parallel to the (211)$_p$ planes. The CBED whole pattern is shown in Figure 6.33 and indicates that the intensity of the (020) reflection was less than the (110) reflection. This CBED pattern matches better with the calculated CBED pattern shown in Figure 6.32 for the O-Ti$_2$AlNb phase, where Ti occupies the 8g sites. Therefore, this match confirms the previous conclusion that Al occupied the 8g sites, rather than Ti, in the proposed ORTH1 phase.

Another result that confirmed that Al occupied the 8g Wyckoff sites in the ORTH1 phase is the observation that the coarse APDBs passed across the interface between the ORTH1 plates and B2 matrix, as seen in Figure 6.25a. From chapter 4, it was shown that Al occupied the 1b sites in the B2 phase, and this left the occupancy of the 1a sites and unfilled 1b sites (~20%) for Nb and Ti. The atoms occupying these sites must have remained in place during the transformation from the B2 phase to the ORTH1 phase, since the APDBs that formed in the β to B2 ordering transition were inherited by the plates. This observation can be seen in Figure 6.34, which shows the APDB vectors of the B2 phase in the (011)$_p$ planes and the ORTH1 phase in the (001)$_o$ planes. These planes are lying parallel to each other, as previously determined from the orientation relationship. From Figure 6.34 it is concluded that the $1/2<111>$ vector present in the B2 phase is transformed into the
Figure 6.33. CBED pattern showing the whole pattern symmetry of the O-Ti$_2$AlNb phase observed in alloy 1.
Figure 6.34. Shows the APDB vectors in the (011)<sub>b</sub> planes of the B2 phase and in the (001)<sub>o</sub> planes of the ORTH1 phase.
1/4[110] vector in the ORTH1 phase. The continuity of the APDB vectors across the B2/plate interface indicates that the occupancy of the atomic sites in the B2 and ORTH1 phases is unaltered during this part of the transformation. Thus, the 1a (Nb/Ti) and 1b (Al) sites in the B2 phase are transformed into the two 4c (4c1 and 4c2) and the 8g sites, respectively, in the ORTH1 phase. Therefore, this result predicts that Al will end up on the 8g sites in the proposed ORTH1 phase.

The results of this study indicated that an ORTH3 phase, different from the proposed ORTH1 phase shown in Figure 6.31, existed during the development of the ORTH1 plates. The ORTH3 phase is believed to exist immediately after the plates formed, when the site occupancy of the B2 phase is locked in, and a disordered occupancy between Nb and Ti on the two 4c sites in the ORTH1 phase had occurred. Proof of this disordered occupancy is obtained by SAED analysis of very thin ORTH3 plates and also by the observation of the columnar shaped APDBs in the ORTH1 plates. The SAED pattern of a very thin plate that had the ORTH3 phase was shown in Figure 6.15. In this pattern, the (hk0) reflections, where h and k are odd integers, are absent for the ORTH3 phase. These same reflections initially appeared as streaks in the SAED pattern of the ORTH2 phase (Figure 6.13), and finally as diffraction spots in the SAED patterns of the ORTH1 phase (Figures 6.9). The columnar shaped APDBs observed in the ORTH1 plate were shown in Figure 6.25 and in the ORTH2 plate in Figure 6.28. The presence of these APDBs indicated that a disorder to order transition occurred and formed two sublattices in the ORTH1 phase. It was previously determined from the structural analysis that the displacement vector of these APDBs was 1/2[100]. This displacement vector as shown in Figure 6.34 connects the 4c1 (Ti) with the 4c2 (Nb) sites in the ORTH1 phase and
is the same displacement vector that has been observed for the APDBs in the O-Ti$_2$AlNb phase [31,34]. Thus, the presence of these fine APDBs indicates that Nb and Ti are initially disordered on the 4c1 and 4c2 sites during the formation of the ORTH1 plates. The implication of this result is that a disordered site occupancy on the 4c1 and 4c2 sites predicts a different ORTH1 structure based on symmetry.

The atomic site occupancy of the ORTH3 phase is determined by considering the inherited site occupancy of the B2 phase and the occurrence of two kinds of lattice distortions. A model for the site occupancy of the ORTH3 phase is created by assuming that the {011} planes of the B2 unit cell is compressed in the <100> direction and expanded in the <011> direction. This is then followed by atomic shuffles of alternating {011} planes to obtain the unit cell shown in Figure 6.35. This figure also shows the unit cell of the ORTH1 phase, but with disordered occupancy between Nb and Ti on the 4c1 and 4c2 Wyckoff sites. The disorder between Nb and Ti indicates that the ORTH3 phase has a different structure and a higher symmetry than the Cmcm symmetry of the ORTH1 phase. The results of this study are consistent with the Pmma space group as the structure for the ORTH3 phase. This conclusion is based on the subgroup/supergroup relations in crystallography that showed that the Pmma space group exists as the minimal non-isomorphich supergroup of the Cmcm space group with its lattice parameters reduced in half along the a and b directions of the ORTH1 phase. The screw axis and the glide plane that exist in the Cmcm structure are retained in the Pmma structure, but with different orientations. This difference in orientation arises from the rotation in the orthogonal axis system which makes the [001] direction in the Cmcm structure the [100] direction in the Pmma structure. Thus, the 2, screw axis is parallel to the [100] direction and the
a-glide plane is parallel to the (001) plane in the Pmma structure. There are two Wyckoff sites in the Pmma structure that evolve from the site occupancy of the B2 phase, and these were the 2e sites at \( \frac{1}{4}, 0, z \) and \( \frac{3}{4}, 0, \bar{z} \) by the Nb and Ti and the 2f sites at \( \frac{1}{4}, \frac{1}{2}, z \) and \( \frac{3}{4}, \frac{1}{2}, \bar{z} \) by Al. The magnitude of the atomic displacements from the \{011\} plane shuffles determined the z coordinates of these two Wyckoff sites and were assumed to be 0.167 for the 2e site and 0.667 (0.167 + 0.500) for the 2f site. Table 6.11 lists the coordinates of the atoms in the proposed ORTH3 phase shown in Figure 6.35.

Figure 6.36 shows a calculated SAED pattern for the ORTH3 phase using the atomic site occupancy given in the model in Figure 6.35. This diffraction pattern was calculated at the [011] zone axis to show that there was consistency with the orientation relationship observed between the ORTH3 and \( \beta \) phases in Figure 6.15. According to the calculated pattern, the [100] and [011] zone axes were parallel and the (011) and (211) planes were parallel. This pattern does not show the systematic rows of (hk0) reflections, where h and k are odd integers, that are observed in the ORTH1 phase. Furthermore, there is good agreement between the structure factors of several reflections shown in Figure 6.36 and the intensity of these reflections observed in the SAED pattern of Figure 6.15. These structural factors and reflection intensities show that the (002) and (011) reflections have similar intensities and that these reflections were greater in intensity than the (001), (010), and (012) reflections. Thus, these results showed that there was good agreement between the calculated and the experimentally obtained SAED patterns of the very thin ORTH3 plates and prove that they have the Pmma structure.
Figure 6.35. Shows the proposed site occupancy of the ORTH3 phase based on the Pmма space group with Nb and Ti atoms occupying the 2e Wyckoff sites and Al atoms occupying the 2f Wyckoff sites.
Table 6.11. The proposed atomic site occupancy of the ORTH3 phase with the Al(Nb/Ti) stoichiometry and the Pmm a (51) space group.

<table>
<thead>
<tr>
<th>Site Number</th>
<th>Site Position</th>
<th>Element</th>
<th>Wyckoff Position</th>
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<td>X</td>
<td>Y</td>
<td>Z</td>
</tr>
<tr>
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<td>0.1667</td>
</tr>
<tr>
<td>2</td>
<td>0.75</td>
<td>0.5</td>
<td>0.8333</td>
</tr>
<tr>
<td>3</td>
<td>0.25</td>
<td>0</td>
<td>0.3333</td>
</tr>
<tr>
<td>4</td>
<td>0.75</td>
<td>0</td>
<td>0.6667</td>
</tr>
</tbody>
</table>

The following Wyckoff values were used:

Al (2f) \( (x, y, z) = (0.25, 0.5, 0.1667) \)

Nb/Ti (2e) \( (x, y, z) = (0.25, 0, 0.3333) \).
Figure 6.36. Shows the calculated SAED pattern of the orientation relationship between the ORTH3 plate and the B2 phase. The OR showed the [100] \text{\textsubscript{O4}} and [011] \text{\textsubscript{B}} zone axes to be parallel and the (011)\text{\textsubscript{O4}} and (211)\text{\textsubscript{B}} planes to be parallel.
6.3.2.3.2 The HCP Phase

The results of this study showed that the HCP plates are structurally similar to the \( \alpha_2'\)-Ti\(_5\)Al (DO\(_{19}\)) phase [10]. The similarities between these two phases included the same Burgers orientation relationship with the \( \beta \) phase, lattice parameters, 1/6\(<11\bar{2}0>\) displacement vector for the APDBs, and P6\(_3\)/mmc space group. These similarities indicate that the atomic site occupancy of the HCP phase is the same as that of the \( \alpha_2'-\text{Ti}_3\text{Al} \) phase, which was previously shown in Figure 2.13. Thus, the atomic site occupancy of the HCP phase is such that the 2d Wyckoff sites are occupied by the Al content and the 6h sites are co-occupied by the Ti and Nb contents of the \( \beta \) matrix in the 1300°C aged sample of alloy 2.

The results showed that the transformation mechanism of the \( \beta \) phase to the HCP plates is similar to that of the \( \alpha_2' \) martensite that has been reported to form in Ti-25Al + Nb (at.%) based alloys [72, 74]. It was shown in chapter 2 that the disordered \( \alpha' \) martensite formed initially upon quenching in the Ti-25Al + Nb alloys and subsequently ordered to form the \( \alpha_2' \) martensite. Therefore, the \( \alpha_2' \) martensite has the same structure and APDBs as does the \( \alpha_2'-\text{Ti}_3\text{Al} \) phase, except that it forms by a martensitic transformation. A similar type of transformation to that of the \( \alpha_2' \) martensite was observed for the HCP plates, since the APDBs observed in these plates (Figure 6.24) were previously found to have a displacement vector of 1/6\(<11\bar{2}0>\). This is the same displacement vector that forms during the ordering reaction from the \( \alpha \)-Ti phase to \( \alpha_2'-\text{Ti}_3\text{Al} \) phase and produces four domains from the 1/6\(<11\bar{2}0>\) translational vectors [78]. This result indicates that the HCP plates form initially with the disordered \( \alpha \) phase, and then they order to the \( \alpha_2 \) phase during water quenching. Thus, the rapid transformation and the ordering of the \( \alpha \) to the \( \alpha_2 \)
The similarity of the structure of the HCP plates to the $\alpha_2$ phase is unexpected due to the high Nb content and the low Ti content of the $\beta$ matrix in the 1300°C aged sample. The composition of the $\beta$ matrix was given in Table 4.1 to be 37Ti-23Nb-40Al (at.%). If it is assumed that the HCP plates form from the $\beta$ matrix with this composition, then the 23%Nb content is greater than the solubility limit of Nb in the $\alpha_2$ phase. The solubility limit has been shown to be $\sim 12\%$Nb in the $\alpha_2$ phase of Ti$_3$Al + Nb alloys [32]. This solubility limit includes the $\alpha_2'$ martensite as well, since the $\sim 12\%$Nb content in these alloys suppresses the formation of the $\alpha_2'$ martensite upon quenching [24, 26, 32]. The stoichiometry of the $\alpha_2$ phase with Ti and Nb sharing the same sublattice and Al occupying the other sublattice shows that the ratio between Ti+Nb and Al to be 3:1. The ratio that was determined for the $\beta$ matrix in the 1300°C aged sample was 3:2 and is different than the stoichiometric ratio. This suggests that the increased Al content in the $\beta$ matrix affects the solubility limit of Nb and raises this limit in the HCP plates.

There are several possible reasons why the HCP plates form, instead of the ORTH1 plates, in the $\beta$ matrix near the $\sigma$ grains at 1300°C. One of the possibilities is that strain was present in the $\beta$ matrix in the regions surrounding the $\sigma$ grains. This strain was expected to have arisen from the volumetric differences between these two phases. This strain is also expected to be large, since the $\sigma$ phase is a topologically close-packed phase [39], while the BCC $\beta$ phase is an open structure with poor packing efficiency. Strain induced by plastic deformation in ferrous materials has been shown to raise the $M_s$ temperature of the martensite transformation [95]. Therefore, the strain that is expected to have formed in the $\beta$ matrix from volumetric
differences with the \(\sigma\) grains could also have raised the \(M_s\) temperature of the plates that formed near the \(\sigma\) grains. It is possible that these plates formed before the \(\beta\) matrix ordered to the B2 phase. This is supported by the result that showed that the APDBs in the B2 matrix did not pass through the HCP plates. Thus, these plates that formed from the disordered \(\beta\) matrix may have then followed a different transformation path compared to the ORTH1 plates, which developed after the \(\beta\) phase ordered to the B2 phase.

It is also possible that composition gradients, developed in the \(\beta\) matrix during the development of the \(\sigma\) grains, favored the formation of the HCP phase over the ORTH1 phase. These composition gradients could have arisen from both the nucleation and the growth stages of the \(\sigma\) grains, since both of these stages required long-range diffusion through the \(\beta\) matrix. The composition gradients are expected to form by the partitioning of elements across the moving \(\sigma/\beta\) interface. From Table 4.1, the most probable elements implicated in the partitioning are Ti and Nb. This is because Nb diffuses to the \(\sigma\) grains, which is a Nb-rich phase, and Ti is partitioned into the \(\beta\) matrix during the development of the \(\sigma\) grains at 1300°C. Likewise, the \(\beta\) matrix was enriched only slightly in Al at 1300°C. This indicates that the solubility limit of Al in the \(\sigma\) phase is similar to the \(\beta\) phase and is \(\sim 40\%\)Al. The increase in Ti and the decrease in the Nb content in the \(\beta\) matrix near the \(\sigma\) grains could have favored the formation of plates with the HCP phases.

An increased Ti content in the \(\beta\) matrix near the \(\sigma\) grains could also have lowered the temperature of the disorder to order transition in the \(\beta\) phase. This idea is consistent with previous studies that have shown that an increase in Nb content raises the temperature of the \(\beta\) to B2 reaction in the Ti\(_x\)Al + Nb alloys [24,25]. Therefore, the opposite behavior is also possible, in which an increase in the Ti
content in the $\beta$ matrix lowers the $\beta$ to B2 reaction temperature. This idea supports the scenario that shows that the formation of the plates with the HCP phase occurred from the disordered $\beta$ phase. Thus, a combination of strain, small differences in composition due to compositional gradients, and a lower temperature for the $\beta$ to B2 ordering reaction may all have contributed to the formation of plates with the HCP phase.

It is suggested that the observation of a third phase in some of the HCP plates indicates an instability in the HCP phase at low temperatures. This idea is based on the concept that when the plates form initially at high temperatures, there is a greater amount of configurational entropy that stabilizes the disordered site occupancy between Nb, Ti, and Al on the 2d Wyckoff site of the $\alpha$-HCP phase. Upon lowering the temperature, these three different atoms then order into two different sublattices which are the 2d site occupied by Al and the 6h site occupied by Ti and Nb to form the $\alpha_2$-HCP phase. This ordering reaction involves a decrease in the configurational entropy and a decrease in the symmetry of the $\alpha$-HCP phase. Likewise, as the configurational entropy is decreased further at lower temperatures, then the composition of the HCP phase can cause an instability in these plates. It is suggested that the instability occurs on the 6h sublattice of the $\alpha_2$-HCP phase, since the $\sim 23\%$ Nb content of these plates is larger than the $\sim 11\%$ to $12\%$ Nb solubility limit that has been reported for Nb in the $\alpha_2$-Ti$_3$Al phase of ternary Ti$_3$Al + Nb alloys. The excess $\sim 40\%$ Al content in the $\alpha_2$-HCP phase is not expected to cause this instability, since Al occupies the 2d site and has been shown in the binary Ti-Al alloys to have a solubility limit in the $\alpha_2$-Ti$_3$Al phase by as much as $\sim 40\%$ Al [10]. Thus, as the temperature is continuously lowered during water quenching, the excess Nb content on the 6h sites shared with Ti causes the instability in the $\alpha_2$-HCP phase.
A structure for this third phase, which will be referred to as $\alpha_3$, is postulated based on the results of the CBED analysis and the subgroup/supergroup relationship between the $\alpha_2$-HCP and $\alpha_3$ phases. From the preceding discussion, lowering the temperature causes a symmetry reduction in the disordered $\alpha$-HCP to ordered $\alpha_2$-HCP transition. This transition involves chemical ordering and has to occur at intermediate temperatures, since the ordering requires thermal activation energy. It is suggested that a similar reduction in symmetry accompanied the transition from the $\alpha_2$-HCP phase to the $\alpha_3$ phase as the temperature is further lowered. The small amount of thermal activation energy at these low temperatures is expected to prevent further chemical exchanges. Thus, this transition must have involved only distortions in the $\alpha_2$-HCP lattice and resulted in the $\alpha_3$ phase.

The structure of the $\alpha_3$ phase was shown by the CBED pattern in Figure 6.7b to have a 3m symmetry axis. The 3m symmetry can only exist in structures based on the cubic and trigonal Bravais lattices. Furthermore, it was found that the SAED patterns of the $\alpha_3$ phase at different orientations were indistinguishable from those of the $\alpha_2$-HCP phase. This observation rules out the cubic Bravais lattice as a possible structure for the $\alpha_3$ phase for the following reason. The SAED pattern of a cubic $\alpha_3$ phase at the [011]$_\beta$ zone axis of the $\beta$ phase shown in Figure 6.6b would have been indexed as the [111]$_{\alpha_3}$ zone axis. Thus, the SAED pattern of the $\alpha_3$ phase at the [111]$_\beta$ zone axis of the $\beta$ phase shown in Figure 6.3a would then have been indexed as the [011]$_{\alpha_3}$ zone axis, since the 35.26° angle that separated the [011]$_\beta$ from the [011]$_\beta$ zone axes of the $\beta$ phase would have also separated the [111]$_{\alpha_3}$ from the [110]$_{\alpha_3}$ zone axes of the $\alpha_3$ phase due to the orientation relationship. The ratio method was used to compare the calculated ratios, based on different lattice parameters that were determined from the [111]$_{\alpha_3}$ zone axis, to the measured ratios which were determined
from the reflections in the SAED pattern of the [110]$_{\alpha_3}$ zone axis. This analysis showed no consistency between the calculated and measured ratios based on the cubic $\alpha_3$ structure. In comparison, the same type of ratio method showed that the trigonal Bravais lattice is possible, since the trigonal unit cell can be indexed using the same (hkl) Miller indices as the HCP unit cell. Furthermore, there are two possible trigonal structures, the P$\overline{3}$m1 and P$\overline{3}1c$ space groups, that are maximal non-isomorphic subgroups of the P6$_3$/mmc space group, which is the space group of the $\alpha_2$-HCP phase [43]. Both of these trigonal space groups contain the necessary 3-fold axis that was observed by CBED analysis. However, the P$\overline{3}$1c space group showed that a c-glide plane is present in the same direction as the c-glide plane in the $\alpha_2$-HCP phase, and that it could have formed by small displacements of Nb and Ti atoms from the 6h Wyckoff sites in the $\alpha_2$-HCP phase. These displacements would have destroyed the 6-fold symmetry in the $\alpha_2$-HCP phase and would have subsequently created the 3 symmetry axis and yet retained the c-glide plane in the $\alpha_3$ phase. Thus, it is suggested that the P$\overline{3}$1c space group is the most probable structure for the $\alpha_3$ phase. However, further work is necessary to confirm this as the possible structure.

6.3.3 Crystallographic Treatment of the Plate Transformation

In this section, it will be shown that the transformations of the ORTH1 and HCP plates occur in a series of transitions that start from the disordered $\beta$ phase and end with either the ORTH1 or HCP phases. Each of these transitions involves a change in symmetry between the parent and product phases that conforms to the subgroup/supergroup relationships in crystallography [43]. This formalism assigns a set of order parameters to the individual transitions and indicates how many variants of the product phase are formed from the parent phase [97]. In this regard, the
results of the structural analysis of the ORTH1 and HCP plates can be used to show these individual transitions, which may then be used to show the entire transformation of these phases as a sequence of transitions.

The results of this study showed that there are two transformation paths for the plates: one that leads to the ORTH1 phase and one that leads to the HCP phase. The two paths are based on the study by Bendersky et al. [33] and are shown in Figure 6.37. The direction of the arrows in the two paths of this figure show whether an increase (up) or decrease (down) in symmetry occurred in the transition of the product phase from the parent phase. The symmetry changes shown by the vertical arrows involve chemical ordering, while those of the inclined arrows involve structural distortions. The bracketed numbers are the order parameters and indicate how many variants of the product phase are formed from the parent phase in the transition.

The discussion that follows will consider these two different transformation paths separately under the sections path 1 and path 2. The results from the structural analysis will be used in support of these paths.

6.3.3.1 Path 1 of the ORTH1 Plates

The results of this study indicated that the ORTH plates developed along path 1 in Figure 6.37. The first transition of this path is consistent with the observations that showed that the APDBs present in the B2 matrix pass through the ORTH1 plates (Figure 6.27a). This result indicates that the ORTH1 plates form from an ordered β (B2) matrix, which implies that the β phase first orders to the B2 phase and then the formation of the ORTH1 plates occurs. Therefore, the development of the ORTH plates begins with the site occupancy of the B2 phase.
Figure 6.37. Shows the two transformation paths that led to the formation of the ORTH1 plates (path 1) and the HCP plates (path 2) from the β phase.
The first transition from the $\beta$ ($\text{Im}3\text{m}$) to the B2 ($\text{Pm}3\text{m}$) phases involves chemical ordering. From the tables of crystallography, the $\text{Pm}3\text{m}$ space group is a type IIa maximal non-isomorphic subgroup of the $\text{Im}3\text{m}$ space group that forms two translational variants [43]. The two variants form the APDBs in the B2 matrix with the $a/2<111>$ displacement vector, as was shown in chapter 4. The implication of the chemical ordering in the $\beta$ phase is that two sublattices form with Al on the 1b Wyckoff site and a disordered mixture of Ti and Nb on the 1a Wyckoff site. Thus, the atomic occupancy of these two sublattices in this first transition remains throughout the rest of the phases along path 1.

The next three transitions, which occur after the B2 phase forms in path 1, are crystallographic descriptions of the plate formation that are consistent with the phenomenological theory of martensitic transformations [79]. These three steps are equivalent to the homogeneous and heterogenous distortions of the classical approach to treating martensitic transformations. Therefore, the three transitions, which are consistent with the homogeneous and heterogenous distortions and the rigid body rotation (see section 6.3.1), are responsible for the formation of the twelve plate variants, the plate morphology (Figure 6.19), and the habit plane (Figure 6.1) of the ORTH1 plates.

The first distortion in the plate development along path 1 of Figure 6.37 is the homogeneous distortion. This distortion is a linear transformation [79] that distorts the unit cell of the B2 phase and forms the unit cell of the Cmmm (base-centered orthorhombic) phase. The unit cells of these two phases and others that follow are shown in Figure 6.38. Following is the crystallographic description of this distortion in space group notation:

\[
\text{Pm}3\text{m} \rightarrow \text{P}4/\text{mmm} + \text{Cmmm}.
\]
The first step formed three variants of the P4/mmm (primitive tetragonal) phase, since the P4/mmm space group is a type I maximal non-isomorphic subgroup of the Pm\bar{3}m space group [43]. These three variants are formed by a compressive distortion in each of the three possible \(<100>_{B2}\) face normals. The second step forms two variants of the Cmmm phase from each of the three tetragonally distorted variants of the P4/mmm phase. This is a tensile distortion that affects all of the atomic positions cooperatively and is accounted for by the relationship that shows the Cmmm space group as a type I maximal non-isomorphic subgroup of the P4/mmm space group [43]. The combination of the compressive and tensile distortions decreases the \([100]_{B2}\) and increases the \([011]_{B2}\) axes in the \((0\bar{1}1)_{B2}\) planes of the Pm\bar{3}m phase (Figure 6.38a) to form the \((010)\) planes of the Cmmm phase (Figure 6.38b).

The site occupancy of the Cmmm phase is determined from that of the B2 phase, since no chemical exchanges occur between the atomic sites during the homogeneous distortion. Taking into account the small distortions, this indicates that the 1a (Nb/Ti) and 1b (Al) sites in the B2 phase are converted into the 2a (Nb/Ti) and 2c (Al) sites in the Cmmm phase [43]. The 2a and 2c Wyckoff sites have fixed coordinates and are at \((0, 0, 0)\) and \((\frac{1}{2}, 0, \frac{1}{2})\), respectively, in the Cmmm phase. The unit cell of the Cmmm phase in Figure 6.38b shows the occupancy of the 2a and 2c sites normal to the \([010]\) axis, since this direction was derived from the \([0\bar{1}1]_{B2}\) axis in the B2 phase (Figure 6.38a). Thus, the base-centered symmetry on the \((001)\) planes of the Cmmm phase are shown to be parallel to the \((100)\) planes of the B2 phase in this figure.

The second distortion, or heterogeneous distortion, involves the transition from the Cmmm phase to the Pmma phase in path 1 of Figure 6.37. The ORTH3 phase was shown previously in the structural analysis discussion to have the Pmma
Figure 6.38. Shows the unit cells of the different structures that led to the formation of the ORTH1 phase from the B2 phase. (a) the B2 (Pm3m) structure; (b) the orthorhombic (Cmmm) structure; (c) the ORTH2 (Pmma) structure; (d) the ordered ORTH1 (Cmcm) structure.
(primitive orthorhombic) structure. Thus, the ORTH3 phase is the Pmma phase that is shown in path 1 of Figure 6.37. This transition consists of the displacement of atoms on alternating (010) planes, or shuffles, in the Cmmm phase. These shuffles can be described using Wyckoff positions and the subgroup/supergroup relation between the Cmmm and Pmma space groups. The Pmma space group is a type IIa maximal non-isomorphic subgroup of the Cmmm space group. This indicates that there are two variants of the lower symmetry Pmma phase that form from the Cmmm phase. The occurrence of the heterogeneous distortion, which displaces atoms on every other (001) plane, transforms the 2a and 2c Wyckoff sites of the Cmmm phase (Figure 6.38b) into the 2e and 2f Wyckoff sites of the Pmma phase. The unit cell of the Pmma phase normal to the [100] direction is shown in Figure 6.38c. The site correspondence between the two phases indicates that Nb and Ti share the 2e sites at \((\frac{1}{4}, 0, z)\) and \((\frac{3}{4}, 0, \overline{z})\) and Al occupies the 2f sites at \((\frac{1}{4}, \frac{1}{2}, z)\) and \((\frac{3}{4}, \frac{1}{2}, \overline{z})\). Thus, the site occupancy of the Pmma phase, which is derived from the B2 phase by changes in symmetry, is the same that was experimentally determined for the ORTH3 phase (Figure 6.36) in the structural analysis discussion.

The two variants of the Pmma phase, that were mentioned previously to have formed from the Cmmm phase, are responsible for the stacking faults present in the ORTH1 plates. These stacking faults were shown in Figure 6.23 to lie parallel to the (001) planes of the ORTH1 plates. The connection between the two variants and the stacking faults was determined by considering the shuffles on alternating (010) planes during the Cmmm to Pmma transition. The direction of the shuffles can occur in opposite [100] directions in the Cmmm phase. This will result in either a positive (+z) or negative (-z) displacement in reference to the unit cell of the Pmma phase. The unit cell of the Pmma phase in Figure 6.38c was constructed with a positive z
displacement and shows an (...ABABA...) type of stacking sequence for the (100) planes. However, a negative z displacement would have created a different stacking sequence and a stacking fault between the two variants. The defect analysis showed that the stacking faults were parallel to (001)$_0$ planes and were visible with all of the g reflections, except for the (002)$_0$ reflection. These observations are consistent with the 1/10<025> displacement vector for the stacking faults and is similar to the vector that has previously been observed in the O-Ti$_2$AlNb phase [31]. The disruption in the stacking sequence of the (001)$_0$ planes due to these faults is similar to that caused by stacking faults in the HCP structures. These changed the stacking sequence of the (0001)$_h$ planes from (...ABABAB..) to (...ABABA|CBCBC..), where | is the stacking fault [98]. These stacking faults originate in the Cmmm to Pmma transition, since the (001)$_0$ planes of the ORTH1 phase are derived from the (100) planes of the Pmma phase. Thus, the stacking faults provided proof of the Cmmm to Pmma transition in path 1.

The last transition in path 1 of Figure 6.37 is responsible for forming the small columnar APDBs observed in the ORTH1 (Figure 6.27b and 6.27c) and ORTH2 (Figure 6.30) plates. From the structural analysis section, it was found that the formation of these APDBs involved chemical ordering between Ti and Nb on two separate 4c Wyckoff sites in the ORTH1 phases, which are connected by the 1/2[100] displacement vector. This same conclusion can be obtained from consideration of the subgroup/supergroup relations and the Wyckoff positions in the Pmma and Cmcm space groups. These two space groups are present in the last transition of path 1. The Cmcm space group is a type IIb maximal non-isomorphic subgroup of the Pmma space group [43]. This subgroup relation indicates that chemical ordering occurs in the Pmma space group that doubles the b and c lattice parameters and forms two
variants of the Cmcm space group. The two Cmcm variants are observed as the fine APDBs in the ORTH1 phases. The CBED analysis showing Al occupying the 8g site in the ORTH1 phase indicates that the chemical ordering involves the 2e Wyckoff site which is occupied by Ti and Nb, and not the 2f site which is occupied by Al, in the Pmma phase. Figure 6.38 demonstrates this result by showing the unit cells and the atomic site occupancies of the Pmma (Figure 6.38c) and Cmcm (Figure 6.38d) phases. When ordering occurs between Ti and Nb, two 4c sublattices are formed in the Cmcm phase. This causes the b and c lattice parameters of the Pmma phase to double in length to form the a and b lattice parameters of the Cmcm phase. This ordering transition results in the alternating occupancies of Ti and Nb along the rows pointing in the [100] direction. The translation vector connecting Ti to Nb along these rows is 1/2[100], which is the displacement vector that is responsible for forming the fine APDBs. Finally, the 2f site in the Pmma phase transforms into the 8g site in the Cmcm phase and is occupied by Al. Thus, this last transition seen in path 1 of Figure 6.37 concludes the development of the ORTH1 plates present in alloy 2.

6.3.3.2 Path 2 of the HCP Plates

The transformation of the HCP phase along path 2 (Figure 6.37) is different from that of the ORTH phase along path 1, since it was found that the HCP plates form from a disordered β matrix. This transformation path was demonstrated by the observation of APDBs in the B2 matrix that did not pass through the HCP plates (Figure 6.24a). The implication of this result is that the disordered sublattice of the β phase is inherited by the plates that form along path 2. This disordered sublattice persists in the subsequent transitional phases of path 2 until the transition from the α to α₂ phases occurs, which involves chemical ordering. The occurrence of this transition was determined from the structural analysis of the APDBs that were
present in the HCP plates. This analysis showed that the displacement vector of these APDBs is $1/6\langle 1120 \rangle$, which is the same vector that forms during the disorder to order transition from the $\alpha$-Ti to $\alpha'_2$-Ti$_3$Al phases [78].

The first three transitions in path 2 of Figure 6.37 describe the homogenous and heterogenous distortions which are consistent with martensitic transformations using symmetry and subgroup/supergroup relations. These three transitions have the same purpose as the three transitions in path 1 that were previously described for the Pm$\overline{3}$m to Pnma phases, except that these transitions involve phases that have a disordered sublattice. Thus, these three transitions which were consistent with the homogeneous and heterogeneous distortions and rigid body rotation (see section 6.3.1) were responsible for the formation of the twelve plate variants, the plate morphology (Figure 6.19), and the habit plane (Figure 6.1) of the HCP plates.

The homogeneous distortion consisted of the first two transitions in path 2 of Figure 6.37. This distortion changes the unit cell of the $\beta$ phase to form the unit cell of the Fmmm (face-centered orthorhombic) phase and is shown in Figure 6.39 along with the other phases that follow in path 2. Following is the crystallographic description of this distortion in space group notation:

$$\text{Im}\overline{3}m \rightarrow \text{I4/mmm} + \text{Fmmm}.$$ 

The first step of the homogeneous distortion forms three variants of the I4/mmm (body-centered tetragonal) phase, which is a type I maximal non-isomorphic subgroup of the Im$\overline{3}$m space group [43]. These three variants are formed by a compressive distortion in each of the three possible $<100>_\beta$ face normals. A tensile distortion in either of the two $<110>$ directions in the I4/mmm phase forms two variants of the Fmmm phase. The distortions in this transition are uniformly applied to all of the atoms in the sublattice, since the Fmmm space group is a type I maximal
non-isomorphic subgroup of the I4/mmm space group [43]. These two transitions formed six plate variants and two more variants formed for each of these six by the rigid body rotation. Thus, this accounts for the twelve plate variants that were observed.

The relationship between the unit cells of the Im\bar{3}m and Fmmm phases after the homogeneous distortion has occurred is shown in Figure 6.39. The unique feature of the site occupancy of the Fmmm phase is differentiated by the 4a Wyckoff sites, since these sites are derived from 2a Wyckoff sites in the β phase. The 4a sites have a disordered site occupancy and are located at the (0, 0, 0) origin and the three face centers. Figure 6.39 indicates that the (001) planes of the Fmmm phase (Figure 6.39b) are parallel to the (0\bar{1}1) planes of the β phase (Figure 6.39a).

The third transition in path 2 of the HCP plates is consistent with the heterogeneous distortion for this martensitic transformation [79]. This transition involves displacements of atoms on alternating (001) planes, or shuffles, in the Fmmm phase. These shuffles can be described with Wyckoff positions and by the subgroup/supergroup relationship between the Fmmm and Cmcm space groups. The Cmcm space group is a type IIa maximal non-isomorphic subgroup of the Fmmm space group and indicates that the atomic displacements are not uniformly applied to all the atoms in the unit cell of the Fmmm phase. There are also two variants of the lower symmetry Cmcm phase that form from the Fmmm phase in this transition. The heterogeneous distortion that causes the displacement of atoms on every other (001) plane transforms the 4a Wyckoff sites in the Fmmm phase into the 4c Wyckoff sites in the Cmcm phase. The coordinates of the 4c sites are (0, y, ½) and (0, \bar{y}, ½) and two more with the (½, ½, 0) lattice translation. These sites have a disordered site occupancy. Therefore, the shuffles are in the [010] direction of the Fmmm phase.
Figure 6.39. Shows the unit cells of the different structures that led to the formation of the HCP phase from the β phase.
(a) the disordered β (Im3m) structure; (b) the disordered orthorhombic (Fmmm) structure; (c) the disordered orthorhombic (Cmcm) and the disordered HCP (P6_3/mmc) structures; (d) the ordered HCP (P6_3/mmc) structure.
and are displaced by an amount equal to $y$ in the $[010]$ direction of the Cmcm phase. The resulting unit cell of the Cmcm phase after these displacements have occurred is shown in Figure 6.38c for the (001) planes.

There are two special conditions that could have arisen in the transition from the Fm3m to the Cmcm phase. The two conditions depend on the magnitude and the direction of the atomic displacements. These two parameters are indicated by the $y$ parameter of the $4c$ Wyckoff site in the Cmcm phase. There are two scenarios that can occur for these special values of the $y$ parameter. If $y$ is equal in magnitude, but opposite in direction for two variants of this transition, then a stacking fault will form between them. However, if $y$ is equal to 0.333, then the Cmcm phase will degenerate into the higher symmetry $P6_3/mmc$ phase, provided that the lattice parameters of this phase have the critical ratio of 0.577, which it does for the hexagonal phase. The results of this study indicated that both of these scenarios occurred during the development of the HCP plates.

The first scenario was indicated by the formation of stacking faults and formed during the Fm3m to Cmcm transition. This was determined by the observation of stacking faults in the HCP plates. The analysis of the stacking faults seen in the plate of Figure 6.23 indicated that they were parallel to the $(0001)_H$ planes and were visible when imaged with all of the $g$ reflections, except the $(0002)_H$ reflection. These observations were consistent with the $1/6<20\overline{2}3>$ displacement vector for the stacking faults and is common for stacking faults in the HCP phases [99]. The stacking faults signified that a disruption in the stacking sequence occurred for the $(0001)_H$ planes from one showing $(..ABABAB..)$ to one showing $(..ABABA|CBCBC..)$, where $|$ is the stacking fault [98]. Thus, these stacking faults
originated in the Fmmm to Cmcm transition, since the \((0001)_{\text{H}}\) planes of the HCP phase are derived from the \((001)\) planes of the Cmcm phase.

The occurrence of the second scenario was indicated by the degeneration of the Cmcm phase into the higher symmetry \(P6_3/mmc\) (\(\alpha\)) phase. This was inferred since the plates that transformed along path 2 consisted of the \(\alpha_{2}\)-HCP phase. As mentioned already, the observation of APDBs with the \(1/6<1120>\) displacement vector indicates that the \(\alpha_{2}\)-HCP plates possesses a disordered \(\alpha\)-HCP structure prior to this ordering reaction. Furthermore, the result that showed that the lattice parameters of the ORTH\(1\) plates formed by quenching from 1300°C had the same \(a/b\) ratio of 0.577 as the HCP phase implied that the condition for hexagonal symmetry was met. The ORTH\(1\) plates develop along path 1 and involve the inheritance of two sublattices from the B2 phase. The two sublattices prevent the Pmma phase from degenerating into a higher symmetry HCP phase, since the HCP phase does not occur as a possible supergroup of the Pmna phase. However, in the case of the HCP plates that develop along path 1, there is the possibility of degeneration into the higher symmetry HCP structure. This is possible because the Cmcm phase of this path possesses a disordered sublattice and does show the \(P6_3/mmc\) as a minimal non-isomorphic supergroup [43].

6.3.4 Formation of Plate Martensite from the \(\beta\) Phase

The structural analysis and crystallographic treatment of the plate martensite in the central portion of the Nb-Ti-Al system suggests that the growth of the plates requires some thermal activation. The thermal activation is required during the formation of both the HCP and ORTH\(1\) plates, since the disorder to order transitions that occur in these plates involve the exchange between different types of atoms into separate sublattices in these structures. The thermal dependency of these
martensite plates is consistent with the formation of martensites in binary Ti-Al and Ti-Nb alloys and in ternary Ti₃Al + Nb alloys, which was covered in chapter 2.

The concept of martensite start (Mₛ) and finish (Mₚ) temperatures is useful to correlate the different orthorhombic (ORTH) structures with the development stages. It was previously shown in chapter 2 that the Mₛ temperature was decreased by the addition of Nb to binary Ti-Nb alloys, but was increased by the addition of Al to binary Ti-Al alloys [73,74]. In ternary Ti₃Al + Nb alloys, the studies have shown that the Mₛ temperature of the α₇' martensite was suppressed to below room temperature for Nb additions greater than ~12at.% [24,26,36]. Thus, martensite plates did not form during rapid cooling in these alloys with high Nb additions. The composition of alloy 2 is 33Ti-27Nb-40Al (at.%) and indicates that the amount of Al is sufficient to compensate for the amount of Nb in raising the Mₛ temperature above room temperature so that the plates could form during rapid cooling. This permits plates that form close to the Mₛ temperature to have more time to thicken than those that form close to the Mₚ temperature, which is below room temperature.

The development of different plate structures for different thicknesses in this study can be interpreted to represent various stages of plate development. This reasoning can be applied to the development of the ORTH1 structure. Since the same habit plane was observed for all of these plates independent of thickness, then this implies that these plates all formed from the β matrix by the same mechanism. The habit plane observed for these plates was consistently found to lie ~11° from the (211)β planes with the plate rotation about the [011]β direction. The results of this study suggest that the ORTH3 plates formed initially from the B2 phase, since these plates were the thinnest. Assuming that the ORTH3 plate formed close to the Mₛ temperature, then this structure can evolve into the ORTH2 phase as the plate
thickens. The observation of small diffuse streaks in the SAED pattern of Figure 6.14 showed proof of this transition. These streaks in the ORTH2 phase were at positions corresponding to a no scattering intensity for the ORTH3 plates (see Figure 6.16), but to diffraction spots for the medium thick ORTH1 plates (see Figures 6.9). If the disorder to order transition from the ORTH3 to ORTH1 structure is complete, then the final development of the ORTH1 structure occurs. Therefore, the ORTH1 structure represents the last stage of development and also correlates with these plates being the thickest of the different ORTH plates.

The ORTH3 plates showing that the Pmma symmetry is considered to be a metastable structure that forms at room temperature. Previous studies have suggested that the Pmma structure played a part in the development of the O-Ti$_2$AlNb phase, but it was not observed [33,34]. Therefore, the composition of the $\beta$ phase in alloy 2, which is inherited by the ORTH3 plates, must have stabilized the Pmma structure. The stability of the Pmma phase was expected to occur at low temperatures, where the thermal activation processes were minimal to prevent the ordering between Ti and Nb atoms onto separate 4c1 and 4c2 sites. The driving force behind this ordering was also expected to have been high because of the different bond strengths between Ti-Al and Nb-Al. However, thermal energy was necessary to drive this ordering reaction, since Nb and Ti had to exchange atomic sites. This reasoning then accounts for the ORTH3 plates being very thin ($\approx 100\,\text{Å}$), since they formed at low temperatures with insufficient thermal energy for ordering to occur.

The ORTH2 plates, that were slightly thicker than the ORTH3 plates, showed streaks developing in the SAED patterns at the (hk0) reflections, where h and k were odd integers. These streaks were caused by the fine APDBs that were formed during the ordering from the Pmma to the Cmcm (ORTH1) structures. They were caused by
small displacements from the correct atomic positions in the Cmcm (ORTH1) structure and indicated that the ORTH2 structure was incommensurate. Therefore, when the Ti and Nb atoms were locked into the correct atomic positions on the 4c1 and 4c2 Wyckoff sites, then the commensurate Cmcm (ORTH1) phase was formed. This commensurate Cmcm phase caused the diffraction spots that were observed in the SAED patterns of the ORTH1 phase (Figure 6.9).

In this study, the HCP plates were found to be the thickest of the different plate structures. This observation is believed to be due to the enrichment of Ti in the composition of the β phase that the HCP plates formed from. The increase in the Ti content of the β phase lowers the disorder to order transition and increases the $M_s$ temperature. Thus, the HCP plates can form from a disordered β matrix and also at a higher temperature than the ORTH plates. This implies a longer development time for the HCP plates than for the ORTH plates and agrees with their larger thickness.
CHAPTER 7
SUMMARY

In summary, the purpose of this investigation was to provide basic research on the phase equilibria and phase transformations in the central portion of the ternary Nb-Ti-Al system, as represented by two alloys with compositions of 27Nb-33Ti-40Al (alloy 2) and 42Nb-28Ti-30Al (alloy 4). Following are the main findings from this study.

The BCC β phase solidified as the primary phase in both alloys 2 and 4. Solid state cooling resulted in the ordering of the primary β phase to the B2 phase, which was metastable at room temperature in these alloys. In alloy 2, solid state cooling also resulted in the formation of the γ-TiAl phase as allotriomorphs and laths along the primary β grain boundaries, plates in the interdendritic regions, and ω-related precipitates in the β matrix.

The precipitation of the σ-Nb2Al phase occurred from the β phase at high temperatures in both alloys 2 and 4. The σ transus was determined to be slightly below 1400°C in alloy 2 and below 1550°C in alloy 4. The σ phase initially formed as isolated grains in the β matrix and along β grain boundaries in both alloys. Several different orientation relationships were observed between the σ and β phases, however, the {110}σ planes were always parallel to the {110}β planes. At lower aging temperatures, the σ phase formed from the β phase as colonies of grains that were similarly oriented along the [001]σ directions. The retained β particles in these
microstructures showed irregular, circular, and elongated morphologies which depended on the formation and growth process of the σ grains.

A eutectoid transformation of the β phase to the σ + γ phases occurred at 1200°C in alloy 2. This transformation was fast and was completed in the RAM sample in less than two minutes. The morphology of the σ + γ two-phase microstructure depended on the heating rate. Slow heating in the vacuum furnace led to the lath morphology, while fast heating in the tube furnace led to equiaxed γ grains in the σ matrix.

A discontinuous transformation of the B2 phase to the σ + β (disordered) occurred at 1000°C in alloy 4. This transformation was still in progress after two minutes of aging, when the sample was subsequently water quenched. The lamellae structure consisted mostly of σ grains and some disordered β particles. An interface was observed between the B2 and β phases at the reaction front. It was assumed that the β phase was metastable and would have transformed with longer aging times to the O-phase, which was based on the O-Ti2AlNb phase. This assumption was supported by the furnace cooling experiments and showed that plates of the O phase formed from the retained β particles.

The β phase transformed completely to the ω-D phase in alloy 2 by either slow cooling from high temperatures or aging at low temperatures. The structural analysis showed that the ω-D phase had the HCP structure and the P6_3/mcm space group. The stoichiometry of the ω-D phase was Al₄Ti₃Nb₂ and was based on the composition of the β phase. The SAED analysis showed that the a lattice parameter was increased and the orientation relationship with the β phase was rotated by 90°, as compared to other ω-related phases reported in this system. It was shown that the
formation of the ω-D phase from the B2 phase occurred by the \{111\}β plane collapse mechanism and involved additional chemical ordering in the atomic site occupancy that was inherited by the B2 phase. The proposed site occupancy of the ω-D phase indicated that the single layers consisted of Al atoms on the 2b Wyckoff site and Nb atoms on the 4d Wyckoff site, while the double layers consisted of Ti atoms on the 6g1 Wyckoff site and Al atoms on the 6g2 Wyckoff site. The transformation path was described using subgroup and symmetry relations as \( \text{Pm3m(B2)} \rightarrow \text{P31m(ω′′)} \rightarrow \text{P6}_3/m\text{cm(ω-D)}. \)

Fast cooling rates from high temperatures resulted in the martensitic transformation of the β phase to plates in alloy 2. Rapid solidification by electromagnetic (EM) levitation and drop quenching resulted in a basket weave appearance in the microstructure of alloy 2 that resembled acicular martensite. The aged samples of alloy 2 that were water quenched also showed the acicular martensite in regions of the microstructure that contained the β phase. The observed habit plane of the plates agreed with that calculated using the invariant line theory. The formation of the martensite plates was thermally activated and involved chemical ordering during quenching. The β composition affected the structure of the plates, and consisted of either the orthorhombic structures with the Pmma and Cmcm space groups, or the HCP structure with the P6_3/mmc space group. The structure of these plates was dependent on thickness. The proposed site occupancy of the ORTH1 structure was based on the Al\(_2\)TiNb stoichiometry, and Al atoms occupied the 8g Wyckoff site, Ti atoms occupied the 4c1 Wyckoff site, and Nb atoms occupied the 4c2 Wyckoff site. Analysis of domain structures, stacking faults, and electron diffraction suggested two possible transformation paths: \( \text{Im3m(β)} \rightarrow \text{Cmcm(disordered)} \rightarrow \)
P6$_3$/mmc(disordered) $\rightarrow$ P6$_3$/mmc(DO$_{19}$) for HCP plates and Pm$\bar{3}$m(B2) $\rightarrow$ Pmma $\rightarrow$

Cmcm(ordered) for orthorhombic plates.
CHAPTER 8
FUTURE WORK

In this study, as in any study, more questions and ideas arise as one finds the answers and solutions to previous questions. Following are some ideas of future work that could be pursued:

1) Determine the transus temperature of the high temperature \( \beta \) phase for other compositions in this central area of the Nb-Ti-Al system. This knowledge is needed for further alloy development, since heat treatments could then be designed that would permit control over the microstructure.

2) Do a systematic study of the competition between the \( \omega \)-D phase and the martensite plate formation in the 27Nb-33Ti-40Al alloy. This study would involve studying the different phonon modes, which were observed as diffuse electron scattering in the diffraction patterns, and how they might affect the transformation of the \( \beta \) phase to each of these structures.

3) Do channel enhanced microanalysis to confirm the atomic site occupancies of the B2 phase, the \( \omega \)-D phase, and the martensite plates that formed in the 27Nb-33Ti-40Al alloy. This would help clarify the role that aluminum may have had on the ordered structures of these phases.
REFERENCES


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BIOGRAPHICAL SKETCH

David Timothy Hoelzer was born June 17, 1959, at Fort Dix, NJ. He was fortunate to be born in a family that was enlisted in the United States Air Force. This allowed him to grow up in foreign countries such as the Philippines and Germany, and in many states in America. He graduated from Tabb High School, VA, in the spring of 1977. He then enrolled at the University of Florida, Gainesville, FL, in the Fall of 1977 and discovered the world of materials science in 1978 as he worked part time in the Materials Science and Engineering Department. When finances became exhausted, he worked for Russ's Sheet Metal in Gainesville, FL, from 1980 to 1982, and gained a valuable skill installing heating and air conditioning systems. He returned to the University of Florida in 1982 and completed his Bachelors Degree in Materials Science and Engineering in 1985. He was admitted to the Graduate School at the University of Florida in 1985. Soon after being admitted into graduate school, he met the former Amy Ann Tuttle whom he married in 1987. In 1991 he received his Masters Degree for research work that was done between 1985 and 1988. He worked on his doctoral research from 1988 until 1991. He was blessed with the birth of his daughter Rachel Lynn in December 1991. In 1992 he became employed at the New York State College of Ceramics, Alfred, NY, where he is still presently employed.
I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Fereshteh Ebrahimi, Chairperson
Associate Professor of Materials Science and Engineering

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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