Study of the Nucleation Mechanism of $\alpha$-Ti in Bimodal and Fully Lamellar Microstructures Developed in the High-Strength, Near-Beta Titanium Alloy, TIMETAL®18

Thesis

Presented in Partial Fulfillment of the Requirements for the Degree Master of Science in the Graduate School of The Ohio State University

By

Adam H. Young

Graduate Program in Materials Science & Engineering.

The Ohio State University

2013

Committee

Hamish L. Fraser, Advisor

William A. T. Clark
Abstract

TIMETAL®18, a high-strength, near-beta titanium alloy, has been introduced recently as a potential replacement alloy for Ti-5553. Near-beta titanium alloys containing slow diffusing constituents could prove beneficial for controlling microstructural features within thick sections. Traditionally, thick sections of near-beta Ti alloys have been processed such that the resulting microstructure is bimodal or duplex in nature, exhibiting an optimal combination of strength and ductility. The work undertaken was focused on microstructural development of this alloy in both the bimodal and fully lamellar microstructures. Microstructural characterization was carried out using an FEI Sirion scanning electron microscope and custom stereological routines developed at the Center for the Accelerated Maturation of Materials (CAMM). Nucleation the of $\alpha$ phase was examined and, with the use of ChemiSTEM™ XEDS and thermodynamic calculations, a small temperature range for significant refinement was estimated corresponding to a pseudospinodal decomposition mechanism. The temperature range for refinement was determined experimentally and the results were compared with those calculated. The results indicate that the pseudospinodal decomposition is a plausible mechanism by which homogenous distributions of $\alpha$ phase may be precipitated in step quenched metastable $\beta$ alloys.
Dedication

This document is dedicated to my family and friends.
Acknowledgments

I would like to thank Prof. Hamish Fraser for his continuous support and guidance throughout my time at OSU. With his help and encouragement I gained skills that I could only obtain at CEOF and CEMAS and a great interest in materials characterization. I would also like to thank everyone in the Prof. Fraser’s research group for their advice, assistance, and sincere friendship during my time with them.
Vita

1987.................................................................Born

2006.................................................................Manchester High School

2011.................................................................B.S. Materials Science & Engineering, The Ohio State University

Publications


Fields of Study

Major Field: Materials Science & Engineering
Table of Contents

Abstract ........................................................................................................................................ ii

Dedication ................................................................................................................................ iii

Acknowledgments .................................................................................................................... iv

Vita ........................................................................................................................................ v

Publications ............................................................................................................................. v

Fields of Study ......................................................................................................................... v

Table of Contents ................................................................................................................... vi

List of Tables ........................................................................................................................ x

List of Figures ......................................................................................................................... xi

Chapter 1: Introduction ............................................................................................................ 1

1.1 History of Titanium ............................................................................................................. 1

1.2 Applications and Usage ..................................................................................................... 1

1.3 Methods for Strengthening ............................................................................................... 3

   1.3.1 Alloying ..................................................................................................................... 3

   1.3.2 Secondary Phase Nucleation ................................................................................... 5
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4</td>
<td>Alloy Classification</td>
<td>8</td>
</tr>
<tr>
<td>1.4.1</td>
<td>α Alloys</td>
<td>9</td>
</tr>
<tr>
<td>1.4.2</td>
<td>α/β Alloys</td>
<td>10</td>
</tr>
<tr>
<td>1.4.3</td>
<td>β Alloys</td>
<td>12</td>
</tr>
<tr>
<td>1.5</td>
<td>Similar Metastable β Titanium Alloys</td>
<td>12</td>
</tr>
<tr>
<td>1.6</td>
<td>Motivation</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>Chapter 2: Experimental Methods</td>
<td>16</td>
</tr>
<tr>
<td>2.1</td>
<td>Material</td>
<td>16</td>
</tr>
<tr>
<td>2.2</td>
<td>Sample Preparation</td>
<td>16</td>
</tr>
<tr>
<td>2.2.1</td>
<td>Sample Preparation for Heat Treatment</td>
<td>16</td>
</tr>
<tr>
<td>2.2.2</td>
<td>Sample Preparation for Electron Microscopy Characterization</td>
<td>16</td>
</tr>
<tr>
<td>2.3</td>
<td>Heat Treatments</td>
<td>17</td>
</tr>
<tr>
<td>2.3.1</td>
<td>Gleeble Heat Treatment</td>
<td>19</td>
</tr>
<tr>
<td>2.3.2</td>
<td>ETMT Heat Treatment</td>
<td>20</td>
</tr>
<tr>
<td>2.4</td>
<td>Characterization</td>
<td>22</td>
</tr>
<tr>
<td>2.4.1</td>
<td>Scanning Electron Microscopy</td>
<td>22</td>
</tr>
<tr>
<td>2.4.2</td>
<td>Focused Ion Beam Milling</td>
<td>22</td>
</tr>
<tr>
<td>2.4.3</td>
<td>TEM/STEM</td>
<td>24</td>
</tr>
<tr>
<td>2.5</td>
<td>Quantification of Microstructural Features</td>
<td>24</td>
</tr>
</tbody>
</table>
2.6 ChemiSTEM™ XEDS ........................................................................................................ 26

2.6.1 K-factor calibration ............................................................................................... 26

2.7 β-Stability and Thermo-Calc Calculations ............................................................... 28

Chapter 3: Results and Discussion ............................................................................... 31

3.1 Microstructural Evolution in Multiple Processing Routes ...................................... 31

3.1.1 β Solution Treated + Quenched to Room Temperature .................................... 32

3.1.2 β Solution Treated + Quenched to Room Temperature + Aging .................. 33

3.1.3 β Solution Treated + Step Quenched + Aging ............................................... 36

3.1.4 α/β Solution Treated + Quenched to Room Temperature + Aging ............... 39

3.2 Microstructural Quantification .............................................................................. 42

3.3 Pathways for α Phase Nucleation .......................................................................... 44

3.3.1 Presence of Athermal ω ..................................................................................... 45

3.3.2 Pseudospinodal Nucleation .............................................................................. 46

3.4 Developing k-factors and Determining Retained β Composition ......................... 47

3.5 Thermo-Calc Free Energy Calculations ................................................................ 49

3.6 Step Quenching Heat Treatments Near Pseudospinodal Temperature ............... 51

3.6.1 Fully Lamellar Step Quenched Heat Treatments .......................................... 51

3.6.2 Bimodal Step Quenched Heat Treatments ...................................................... 55

3.7 Mechanical Properties Near Pseudospinodal Temperature ................................. 59
Chapter 4: Conclusions and Future Work................................................................. 61

References ..................................................................................................................... 64
List of Tables

Table 1: Weight percent alloying content for some similarly \(\beta\)-stabilized \(\beta\) titanium alloys ........................................................................................................................................... 13

Table 2: Heat treatment schedule.................................................................................................................. 18

Table 3: XEDS determined composition and calculated \(\beta\)-stability.......................................................... 48
List of Figures

Figure 1: Effect of various alloying additions on phase diagrams [1]............................. 4
Figure 2: Metastable phase diagram ................................................................................. 7
Figure 3: Titanium isomorphous phase diagram alloy classification [1]............................ 9
Figure 4: Gleeble environmental chamber and resistive heating grips......................... 19
Figure 5: ETMT environmental chamber and resistive heating grips ............................. 20
Figure 6: Schematic heat treatment processing routes.................................................... 21
Figure 7: FIB foil creation ............................................................................................... 23
Figure 8: MIPAR image processing ................................................................................. 25
Figure 9: As-received TIMETAL®18 in the bimodal starting condition ......................... 32
Figure 10: 910°C for 15 minutes + quenched to room temperature ............................... 33
Figure 11: 910°C + quenched to room temperature + 500°C for 2 hours + quench....... 34
Figure 12: 910°C + quenched to room temperature + 600°C for 2 hours + quench....... 35
Figure 13: 910°C + quenched to room temperature + 700°C for 2 hours + quench....... 35
Figure 14: 910°C + quench to room temperature + 800°C for 2 hours + quench ......... 36
Figure 15: 910°C + step-quenched to 600°C for 2 hours + quench................................. 37
Figure 16: 910°C + step-quenched to 700°C for 2 hours + quench................................. 38
Figure 17: 910°C + step-quenched to 800°C for 2 hours + quench................................. 38
Figure 18: As-received material + 500°C for 2 hours + quench..................................... 40
Figure 19: As-received material + 600°C for 2 hours + quench................................. 41
Figure 20: As-received material + 700°C for 2 hours + quench................................. 41
Figure 21: As-received material + 800°C for 2 hours + quench................................. 42
Figure 22: Mean linear intercept of the quenched to room temperature + aged samples. 43
Figure 23: Volume fraction of $\alpha$ phase in quenched to room temperature + aged samples
........................................................................................................................................... 44
Figure 24: [110] diffraction pattern with $\omega$ satellite reflections ....................................... 45
Figure 25: [110] diffraction pattern and corresponding dark field image .................. 46
Figure 26: Calculated $\alpha$ and $\beta$ phase free energy curves at 640°C ......................... 49
Figure 27: Calculated $\alpha$ and $\beta$ phase free energy curves at 590°C ......................... 50
Figure 28: 910°C + step quenched to 650°C for 2 hours + quench............................... 51
Figure 29: 910°C + step quenched to 640°C for 2 hours + quench............................... 52
Figure 30: 910°C + step quenched to 630°C for 2 hours + quench............................... 52
Figure 31: 910°C + step quenched to 620°C for 2 hours + quench............................... 53
Figure 32: 910°C + step quenched to 610°C for 2 hours + quench............................... 53
Figure 33: 910°C + step quenched to 600°C for 2 hours + quench............................... 54
Figure 34: Mean linear intercept of $\alpha$ laths in fully lamellar microstructures ............. 55
Figure 35: 810°C + step quenched to 650°C for 2 hours + quench............................... 56
Figure 36: 810°C + step quenched to 630°C for 2 hours + quench............................... 56
Figure 37: 810°C + step quenched to 610°C for 2 hours + quench............................... 57
Figure 38: 810°C + step quenched to 590°C for 2 hours + quench............................... 57
Figure 39: Mean linear intercept of $\alpha$ laths in bimodal microstructures......................... 59

xii
Figure 40: Vickers hardness of fully lamellar microstructures ........................................ 60

Figure 41: Vickers hardness of bimodal microstructures .................................................. 60
Chapter 1: Introduction

1.1 History of Titanium

Although titanium was first discovered by William Gregor in 1791 and Martin H. Klaproth in 1795, the field of titanium metallurgy did not materialize until an economical method for titanium extraction was implemented. Titanium is the fourth most abundant element in the earth’s crust and exists in oxide form primarily in Rutile (TiO$_2$) and Ilmenite (FeTiO$_3$) ores. In 1940 William J. Kroll published “The Production of Ductile Titanium,” which described the electrochemical process he employed to produce titanium from titanium ores. Shortly after the introduction of the Kroll process, titanium and titanium alloys were seen as the material of choice for aerospace applications because of their low density, high strength, corrosion resistance, and fracture toughness. While titanium has a set of highly-desirable properties, its use has been limited to high value-added applications because of the high cost of producing elemental titanium, alloying, and machining finished products.

1.2 Applications and Usage

Titanium and titanium alloys have been used in a number of applications that exploit any number of their physical properties. In terms of tonnage, titanium alloys are most often utilized in the aerospace industry for airframe structures and in turbine engines. Interestingly, titanium is seeing an increase in use as separator on the new 787 Dreamliner, in part because of the electrochemical incompatibility of aluminum and carbon fiber matrix composites, which create a galvanic couple when joined.[1]
Titanium alloys are also used extensively in the biomedical field, where corrosion resistance, biocompatibility, and physical properties make them very desirable for implant devices that replace failed hard tissue. Some examples include hip, shoulder, and knee replacements, and a number of other applications in dental hardware. Titanium use has increased, not only because of biocompatibility, but also because of the low modulus of titanium relative to other metallic implant alloys, such as stainless steels and Co-based alloys. In load-bearing applications such as a hip replacement, the elastic modulus of the implant plays a role in adhesion to the bone in contact with the implant. Differences in elastic modulus result in shear stresses at the interface of the bone and implant and can lead to premature failure. For this reason, low modulus alloys specifically designed for biomedical applications are being developed.

Other applications include use in petrochemical plants where corrosion resistance is the most important factor in material selection. In most of these applications, commercially pure titanium alloys can be used in a number of different grades depending on physical property needs. These CP titanium grades refer to interstitial content, primarily oxygen, in the alloy that can increase strength without the development of secondary phase nucleation for strengthening. Other applications, such as sports equipment, are typically designed to exploit the high specific strength of titanium alloys. In cycling Ti-3Al-2.5Sn is used because of its low weight and weldability, which is useful in low-density welded bicycle frames and other structures. Many different alloys have been developed for specific applications and this can be contributed to the tailorability of titanium alloys. Microstructural and chemical aspects of titanium make
the use of alloying elements for both solid solution strengthening and secondary phase precipitation strengthening very valuable. That coupled with an understanding of the many different microstructures, and their affect on properties, in these alloy systems make titanium alloys very attractive in terms of alloy development.

1.3 Methods for Strengthening

Titanium alloys can be strengthened by solid solution strengthening, precipitation hardening, increasing dislocation density, and grain boundary hardening [1]. Titanium has two different crystal structures: hexagonal close packed, α phase, at low temperature, and body centered cubic, β phase, at high temperature. In pure titanium the transition temperature is 882°C, but can be shifted significantly by alloying. Solid solution strengthening can be used to strengthen either the α phase or β phase. In commercial alloys, the use of alloying additions can be used to raise or lower the α/β transition temperature and stabilize either phase. Solid solution strengthening may also be accomplished either by occupying interstitial or substitutional lattice sites. In some alloys β stabilizing elements are added to retain the β phase at room temperature if fast cooling is used to lock the phase in a metastable state. This leads to the utilization of different processing routes to develop different microstructures through nucleation of secondary phases in a number of morphologies.

1.3.1 Alloying

The alloying elements used in titanium alloys can be broken up into two main categories, α stabilizing elements and β stabilizing elements. The elements are grouped into either category based on the effect they have on the α/β transformation temperature,
with $\alpha$ stabilizers raising the transformation temperature, therefore stabilizing the $\alpha$ phase, and $\beta$ stabilizers lowering the transformation temperature, therefore stabilizing the $\beta$ phase. While a number of elements are known to stabilize the $\alpha$ phase, only a few are used in titanium alloying.

![Effect of various alloying additions on phase diagrams](image)

Figure 1: Effect of various alloying additions on phase diagrams [1]

Aluminum and the interstitial $\alpha$ stabilizers O, N, and C are the main $\alpha$ stabilizers. Aluminum is the most used $\alpha$ stabilizer because it has a large solubility in both phases. It is a relatively cheap alloying element, and its effect on properties is more easily controllable than O, N, and C. Oxygen is the main alloying element in CP grades of titanium because very small amounts of oxygen significantly stabilize and strengthen the $\alpha$ phase. Titanium alloys are melted under vacuum because of their affinity for oxygen. Titanium heated in air will develop an $\alpha$ case that is very high in oxygen, which significantly lowers ductility and could act as the brittle site at which surface cracks form.

The $\beta$ stabilizing element can be classified in two distinct categories, the $\beta$ isomorphous group and the $\beta$ eutectoid group. The $\beta$ isomorphous elements lower the
α/β transformation temperature, but the addition of these elements does not result in secondary phase precipitation upon cooling to room temperature. As shown in Figure 1, the effect of adding β isomorphous alloying elements will simply stabilize the β phase and, beyond a critical amount of alloying additions, it is possible to retain β phase stability at room temperature. The β eutectoid elements also stabilize the β phase, but at room temperature the α phase and another ordered phase will be stable [2].

TIMETAL®18 consists of the α stabilizers Al and O, the β isomorphous stabilizers V and Mo, and the β eutectoid stabilizers Fe and Cr, along with a number of other trace elements. TIMETAL®18 has an α/β transformation temperature of about 863°C and it is considered a metastable β or near-β alloy because of the amount of alloying content it contains, and because it can completely retain β (or more appropriately, suppress α nucleation) when quenched to room temperature.

1.3.2 Secondary Phase Nucleation

Several phase transformations are of interest in titanium alloys, but the phenomena that cause structural phase transformations in titanium alloys are not all well understood. The pathway for α nucleation in a β titanium matrix is of specific interest. The precipitation of hcp α in a bcc β matrix that takes place during cooling from the β phase field into the α + β phase field follows a burgers orientation relationship [3]. The α phase is oriented relative to the β phase where

\[(0001)_α // (110)_β\]
\n\[[1\bar{2}0]_α // [111]_β\]
In metastable $\beta$ titanium alloys there are two metastable phases that form upon quenching from the $\beta$ phase field. They are the $\omega$ and $\beta'$ phases. The $\beta \rightarrow \omega + \beta$ and the $\beta \rightarrow \beta' + \beta$ transformations take place because of a miscibility gap in these alloy systems. The $\beta'$ phase will form in more heavily $\beta$ stabilized alloys, while the $\omega$ phase will form in less $\beta$ stabilized alloys, as can be seen in Figure 2.

The $\omega$ phase can be precipitated in two manners. The athermal $\omega$ phase is formed as 1 to 2 nm precipitates periodically spaced along $<111>_{\omega} /[0001]_{\omega}$ during rapid quenching from above the $\omega$ phase field, and has been shown to form at a critical $\omega_s$ temperature and increase in volume fraction with decreasing temperature [4]. The athermal $\omega$ is oriented relative to the parent $\beta$ phase such that

$$(0001)_{\omega} // (111)_{\beta}$$

$$[2\overline{1}\overline{1}0]_{\omega} // [\overline{1}\overline{1}0]_{\beta}$$

This athermal $\omega$ has a hexagonal structure with a $c/a$ ratio of 0.613 [5]. The second type of precipitation occurs during heat treatment in the $\omega + \beta$ phase field. This form of $\omega$ is referred to as isothermal $\omega$ and will have a trigonal crystal structure [6].

It has been suggested that the homogenous distribution of $\alpha$ phase nucleation may occur with influence from $\omega$ or $\beta'$ precipitates as precursors [1, 7, 8]. Utilizing these phase transformations would require a material processing route that includes solution treatment above the $\alpha/\beta$ transus, quenching to room temperature, and then a subsequent step would be taken to heat the material up to an intermediate temperature in the $\alpha + \beta$ phase field to nucleate $\alpha$ precipitates. If the $\alpha$ phase could be precipitated in a refined distribution without the need for precursors, then the processing route could be
augmented so that the material is solution treated and step quenched directly to the final temperature for $\alpha$ phase precipitation.

![Metastable phase diagram](image)

**Figure 2: Metastable phase diagram**

The $\omega$ phase and $\beta'$ phase are thought to dissolve above about 450 - 500°C depending on alloy chemistry [8, 9]. If the presence of the $\omega$ or $\beta'$ phase were required as a precursor for homogeneous $\alpha$ phase nucleation, step quenching from the solution treatment temperature to an aging temperature above the $\omega + \beta$ or $\beta' + \beta$ phase field would not result in homogenous $\alpha$ phase nucleation. Homogeneous $\alpha$ phase nucleation can be achieved through thermal processing above these phase fields and the mechanism responsible is not well understood. The nucleation of fine $\alpha$ laths homogeneously in a $\beta$ matrix may be the result of a pseudospinodal decomposition reaction. Ni and Khachaturyan recently introduced the concept of pseudospinodal decomposition as a
means to explain the production of periodic coherent nanoscale microstructures that are produced from the decomposition of alloys with a cubic \( \rightarrow \) tetragonal transformation [10]. The pseudospinodal transformation involves the decomposition of a homogeneous parent phase into two subsequent phases that continuously change in composition until reaching their equilibrium composition [11]. It has been proposed that, in titanium alloys, small composition fluctuations in the matrix may lead to precipitation of coherent particles that will then proceed to equilibrium compositions by diffusion of either \( \alpha \) or \( \beta \) stabilizing elements to their respective phases.

1.4 Alloy Classification

Titanium alloys can be grouped into several categories based on the amount of alloying content in each alloy, as well as the type of achievable microstructures in each alloy. In general, they can be classified into \( \alpha \), \( \alpha/\beta \), and \( \beta \) alloys. Both the \( \alpha \) and \( \beta \) alloys can be split up into CP, \( \alpha \), and near-\( \alpha \) in the case of \( \alpha \) alloys and near-\( \beta \), metastable-\( \beta \) and stable-\( \beta \) in the case of \( \beta \) alloys. The differences between each can be represented schematically as shown in Figure 3.
Figure 3: Titanium isomorphous phase diagram alloy classification [1]

TIMETAL®18 has enough β stabilizer content to retain β phase when quenched to room temperature, where it is in a metastable state. A secondary heat treatment higher up in the α + β phase field will result in the nucleation and growth of the α phase. The hold temperature and the heating and cooling rates used in the secondary heat treatments will affect the morphology of the resulting microstructure.

1.4.1 α Alloys

This class of alloys is comprised almost entirely of the hcp α phase. Alloys in the α alloy class are preferentially used for applications where weldability, cold workability, low service temperature and corrosion resistance are major design considerations. Because the α phase is the low temperature phase in titanium, heat from welding processes or processes that produce heat in the material do not nucleate secondary phases as would be expected in β alloys. Because of their insensitivity to thermal processing, α
are used for welded structures. Cold working of the hcp phase will reduce ductility, but combinations of cold working and annealing make some α titanium alloys desirable for forming operations such as tube forming [2]. The poor low temperature deformation characteristics of the bcc phase make β alloys undesirable for low service temperature applications, so α alloys are used for cryogenic applications.

Cold working and solid solution strengthening are the typical methods used to harden α alloys. Even in CP titanium there is some amount of Fe that will result in a small amount of β phase retention at room temperature. In CP and α titanium alloys, small amounts of β phase can be used to pin grain boundaries and reduce grain growth during annealing so that the resultant microstructure has a smaller grain size, which leads to a higher strength according to the Hall-Petch relationship [1].

1.4.2 α/β Alloys

These alloys are capable of higher strengths than α titanium alloys; have a good combination of properties; respond well to a number of processing methods; and can be used in service temperatures up to 400°C [12]. The α/β alloys are used in a wide range of applications because of the combination and tailorability of mechanical properties. There are 4 microstructural conditions associated with thermo-mechanical processing routes, in which α/β titanium alloys are typically produced.

The first condition is the mill annealed condition, wherein the material is homogenized above the α/β-transus, cooled to room temperature, worked at an elevated temperature in the α/β phase field, cooled to room temperature, annealed at an intermediate temperature, and then cooled to room temperature. This processing route
leads to a microstructure that is bimodal, with equiaxed and lamellar α, but may contain indications of cold or hot working such as tracers [13]. The second condition is the recrystallization annealed condition, which is similar to the mill annealed condition except the last annealing stage takes place at a higher temperature. From this hold temperature the material is slow cooled to result in microstructure with a large amount of equiaxed α and a small amount of lamellar α which leads to a small drop in strength, improved fracture toughness, and crack growth resistance [14].

Another condition is the β annealed condition. It is produced from a processing route similar to the recrystallization anneal, except the anneal stage is done above the α/β-transus temperature yielding complete recrystallization and β grain growth. This condition is used for maximizing the fracture toughness of the material. The strength level is the lowest of the four conditions but it is the most damage tolerant. The final condition is the solution treated and aged condition, which is produced by solution treatment in the β phase field, cooling to room temperature and aging at an intermediate temperature within the α + β phase field. This process produces the highest strengths of the four microstructural conditions [14]. It is important to point out that within each of these processing routes the heating and cooling rates and heat treatment temperatures all play a role in the final microstructure. In β alloys there are two conditions that are of interest in this work, the bimodal condition and the β-processed condition, which will be talked about further in section 1.4.3.
1.4.3 β Alloys

This class of alloy differs from α/β and α alloys because the β phase can be retained to room temperature and secondary heat treatments can be used to precipitate a very fine distribution of α phase laths. Because of the precipitation of a very fine homogenously distributed secondary phase, β titanium alloys can be hardened to very high yield strengths. When these alloys are forged before heat treatment in a retained β condition without the precipitated α phase they have a much lower flow stress, which enables very good formability. After forming operations they can be heat treated to produce a final forged product in a high strength condition. This processing route is generally referred to as β-processed and it yields the highest strength levels but with low ductility. Multiple examples of β-processed microstructures can be seen in Section 3.1.2. To increase the ductility of forged products, the bimodal condition is used in β titanium alloys. The bimodal condition involves working in the α + β phase field, followed by cooling to room temperature to produce a β matrix with a dispersion of equiaxed α phase. The alloy will then be heat treated just as the β-processed condition is, but with the end result being a mixture of larger equiaxed α phase and smaller lath α phase. Examples of the bimodal microstructure can be seen in Section 3.1.4. This processing route yields higher ductility, while trading a minimal amount of tensile strength.

1.5 Similar Metastable β Titanium Alloys

The first significant β alloy developed in the 1950’s and 1960’s was Ti-13V-11Cr-3Al for use in the SR-71[14]. This heavily β-stabilized alloy was developed for use at elevated temperatures where thermal stability was a key design metric. Although the
use of this alloy was considered a great success in terms of the SR-71 effort, its low ductility and difficult processing considerations were impetus for increased research and development of other β-titanium alloys. In the present work the $\beta \rightarrow \alpha$ transformation is of specific interest. It is necessary to review literature that details work on alloys with similar phase transformations. VT22 and TIMETAL®555 are of specific interest because they are predecessors to TIMETAL®18; β-titanium alloys with similar phase transformations, such as Ti 10-2-3 and Ti 15-3, are also of interest.

The compositions shown in Table 1 are given so that the Molybdenum Equivalence is about the same for each alloy. β titanium alloys can be split up into β-rich α/β alloys, metastable β alloys, and stable β alloys when the overall β stability is below 8 wt%, between 8 and 30 wt%, and above 30 wt%, respectively, as outlined in Section 2.7 [15]. By this classification all of the alloys in Table 1 are metastable β alloys. Although the use of each alloy in multiple forms has occurred, alloys in Table 1 are typically used as forging alloys with the exception of Ti 15-3, which is typically used in strip product forms [16].

Table 1: Weight percent alloying content for some similarly β-stabilized β titanium alloys.
Understanding the use of similarly stabilized alloys is important because differences in the amount of β stabilizers will cause differences in the β phase stability and may have an affect on the recrystallization and precipitation reactions [17]. By definition, these metastable β alloys retain β phase in a metastable state when quenched to room temperature. In the quenched form β titanium alloys can be extensively cold worked and, after heat treatment, strength levels as high as 1.7 GPa can be achieved [15]. It is through the precipitation of different α phase morphologies that metastable β titanium alloys can achieve such a wide range of mechanical properties. The alloys in Table 1, with the exception of Ti-15-3, are used for thick forged components. Accurate means to understand microstructure/property relationships are of specific interest in large parts where interior and exterior cooling and heating rates vary greatly. The β → α phase transformation is key to the types of microstructures developed and a complete understanding of the mechanisms involved will be an important tool in alloy design.

The alloys in Table 1 have been shown to exhibit athermal ω formation [1, 7, 18]. The formation of the athermal ω phase has been shown to increase with decreasing β stabilizer content and the high diffusivity of iron has also been shown to enhance precipitation in metastable β alloys [17]. In Ti-V and Ti-Mo systems, adding Al or O will reduce the stability of ω precipitates by stabilizing the α phase, and Zr and Sn additions act to limit the volume fraction of ω phase by stabilizing the β phase [19]. It has additionally been suggested that compositional fluctuations in the β phase of Ti-V alloys can lead to an increase in the driving force for α phase precipitation, but formation of the athermal ω phase is not associated with compositional fluctuations [20]. Athermal
also forms in Ti-LCB (Ti-6.8Mo-4.5Fe-1.5Al). In a study by Jacques et al., the microstructure from a quenched-to-room-temperature and a step-quenched Ti-LCB sample that were aged at the same temperature were said to have no major differences in microstructure [21].

1.6 Motivation

The motivation for this work was to probe the types of microstructures that could be achieved and to understand the nucleation of α phase in these alloys, as well as how that could affect processing parameters. The use of CAMM-developed MIPAR for stereology has enabled the rapid quantification of microstructural features. In order to predict the microstructural refinement from the compositionally dependent thermodynamic calculations, in the retained β phase region of a bimodal microstructure precise XEDS was needed. SEM XEDS systems generate x-rays from the bulk of the sample, and, in a material with a well dispersed and large number of equiaxed α particles, the generation of x-rays from bulk may contain compositional information from both the α and β phase. ChemiSTEM XEDS has opened up the possibility of site specific chemical information from thin foils, with good statistics which can be used to approximate the thermodynamic propensity for α nucleation. This coupled with MIPAR can be used to find valuable information about phase nucleation that can help guide processing schedules.
2.1 Material

The bulk of the work was done using samples excised from the mid-radial region of a 6-inch diameter bar of TIMETAL®18 which was supplied by TIMET. This material was used for heat-treatment experiments in a Gleeble™ 1500 thermo-mechanical simulator and an Instron® ETMT, Electro-Thermal Mechanical Tester. The heat treated material was then characterized using a number of methods.

2.2 Sample Preparation

2.2.1 Sample Preparation for Heat Treatment

In order to keep the starting microstructure and heat treatment processes consistent, samples were created for both the Gleeble and ETMT with the same sample geometry from the same region of bar. The sample geometry of heat treatment samples was 40×3×1.5mm. They were cut from the bar using an EDM at Jett Industries, Inc. Samples had an EDM recast layer on the surface that was removed to avoid oxygen contamination during heat treatment and to allow better contact with the grips of the resistive heating furnaces.

2.2.2 Sample Preparation for Electron Microscopy Characterization

The sample preparation for scanning electron microscopy was that of typical metallurgical preparation procedures, which include mounting, grinding, and polishing. After the heat treatment, samples were sectioned with an EDM leaving a length of about 5mm oriented such that the narrow dimension of the bar was parallel with the mount surface. Multiple samples were cut in this orientation and then mounted together in
KonductoMet® conductive mounting media, leaving a single mount with 3 to 5 samples, where each sample experienced different heat treatment schedules. The mounts were then labeled and polished using Allied High Tech Products, Inc. polishing media. Each mount was polished using 320, 400, 600, and 800 grit papers followed by 24 hours in a vibratory polisher filled with 0.05 µm colloidal silica. The mount was then cleaned thoroughly using distilled water, isopropyl alcohol and micro organic soap.

2.3 Heat Treatments

The heat treatment schedule was created in order to investigate the development of microstructures in both the bimodal and β-processed starting conditions. Two processing routes were investigated. The first was quenching from the processing temperature to room temperature, and then heating to the final heat treatment temperature. The second was step quenching from the processing temperature to the final heat treatment temperature.
Table 2: Heat treatment schedule

<table>
<thead>
<tr>
<th>Starting Solution Treatment</th>
<th>Intermediate Cooling</th>
<th>Aging Treatment</th>
<th>Final Cooling</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beta Tran -50°C</td>
<td>water quench</td>
<td>500°C/2hr</td>
<td>water quench</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>700°C/2hr</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>600°C/2hr</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>600°C/2hr</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>500°C/2hr</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>500°C/2hr</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>400°C/2hr</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>400°C/2hr</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>300°C/2hr</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>Step quench</td>
<td>750°C/2hr</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>700°C/2hr</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>650°C/2hr</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>50°C/2hr</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>620°C/2hr</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>610°C/2hr</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>600°C/2hr</td>
<td>&quot;</td>
</tr>
<tr>
<td>Beta Tran +50°C</td>
<td>water quench</td>
<td>500°C/2hr</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>800°C/2hr</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>700°C/2hr</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>700°C/2hr</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>600°C/2hr</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>600°C/2hr</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>500°C/2hr</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>500°C/2hr</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>400°C/2hr</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>400°C/2hr</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>Step quench</td>
<td>750°C/2hr</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>700°C/2hr</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>650°C/2hr</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>640°C/2hr</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>620°C/2hr</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>610°C/2hr</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>600°C/2hr</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

Note: Water Quench ≈ 300°C/2hr; Beta Tran ≈ 865°C
2.3.1 Gleeble Heat Treatment

Heat treatments were carried out on a Gleeble™ 1500 thermo-mechanical simulator. None of the heat treatments incorporated any form of deformation. The Gleeble was equipped with an environmental chamber and all heat treatments were performed under vacuum. Each test sample was polished with 320, 400, and then 600 grit papers to remove any EDM layer in order to prevent contamination. An R-type thermocouple was spot welded to the center of the sample. The thermocouple was used to monitor the temperature, in order to control the current used resistively heat the sample. Careful preparation and adequate contact allowed the Gleeble controller to maintain temperature within ±1°C. For consistency all samples were heated at a rate of 10°C/s and cooled at approximately 30°C/s. Cooling was accomplished by cutting power and allowing the water cooled grips to extract heat.

Figure 4: Gleeble environmental chamber and resistive heating grips
2.3.2 ETMT Heat Treatment

Heat treatments were carried out on an Instron® ETMT, Electro-Thermal Mechanical Tester. None of the heat treatments incorporated any form of deformation. The ETMT was equipped with an environmental chamber and all heat treatments were performed under vacuum.

Figure 5: ETMT environmental chamber and resistive heating grips

Each test sample was polished with 320, 400, and then 600 grit papers to remove any EDM layer in order to prevent contamination. An R-type thermocouple was spot welded to the center of the sample. The thermocouple was used to monitor the
temperature in order to control the current used to resistively heat the sample. For consistency all samples were heated at a rate of 10°C/s and cooled at approximately 30°C/s. Cooling was accomplished by cutting power and allowing the water cooled grips to extract heat. Although the ETMT has a different grip design, the same cooling method was used, resulting in an approximately 30°C/s cooling rate. Both the Gleeble and ETMT were used for heat treatments for the purpose of examining processing routes and nucleation of α phase. Schematic representations can be seen in Figure 6.

Figure 6: Schematic heat treatment processing routes
2.4 Characterization

After metallographic preparation, the samples were imaged using an FEI Sirion SEM. Multiple images were taken of the microstructure in order to create a data set with enough microstructural features for microstructural quantification. The area fraction of the equiaxed $\alpha$ phase, the area fraction of lath $\alpha$ phase, the total area fraction of $\alpha$ phase, and mean linear intercept of $\alpha$ laths were quantified. In order to investigate the nucleation process, an FEI Helios Dual-Beam FIB was used to excise and thin samples from the surface for imaging in a Philips CM200 TEM and XEDS in an FEI Image Corrected Titan S/TEM.

2.4.1 Scanning Electron Microscopy

Samples mounted in conductive mounting media were prepared metallographically and cleaned before examination. A standard microscope setup was used in order to produce consistent images across the different types of microstructures for quantification. Backscattered electron images were taken at an accelerating voltage of 15kV with a spot size 4 at a working distance of 4 mm. For quantification, 5 representative images were taken of each microstructure to be quantified using MIPAR, an image processing and microstructural quantification program developed at CAMM.

2.4.2 Focused Ion Beam Milling

In order to create site-specific foils for TEM examination, the Helios Dual-Beam FIB was used to excise and then thin FIB foils for use in the TEM. The Helios utilizes a gallium source ion column as well as an electron column for imaging. Platinum is
deposited along the area of interest to protect the region below it from ion damage. The platinum is introduced in a large molecule gaseous compound that is broken up when ions from the gallium source bombard them. The gallium ion column is used to accelerate ions towards the surface of the material in order to mill, or remove, the material. The FIB foil can then be removed from the surface with an Omni-Probe micromanipulator that allows for precise movements. The Omni-Probe is attached to the FIB foil by depositing platinum to weld the two pieces together. The foil extraction process can be seen in Figure 7. After the FIB foil has been removed, it is welded to an Omni-Probe grid and thinned. The FIB foil is cut to electron transparency by orienting it so that the ions remove material in a manner to thin the foil. After the bulk thinning at 30kV has been done, a lower accelerating voltage is used to clean the surface of the foil. A final cleaning step is used to remove as much ion damage as possible, by using a low energy Nanomill in order to remove any redeposited or ion damaged material.

Figure 7: FIB foil creation
2.4.3 TEM/STEM

The pathway for the nucleation of α phase was examined using a Philips CM200. In order to determine whether the presence of ω phase took place in this alloy system, as well as to determine the lower limit of cooling rate to suppress α phase nucleation when cooling to room temperature, dark field images and corresponding diffraction patterns were taken. An FEI Titan equipped with ChemiSTEM XEDS was used to calculate k-factors for TIMETAL®18 and to determine the composition of retained β phase in an α/β starting microstructure.

2.5 Quantification of Microstructural Features

Sets of micrographs from each microstructure were used to determine the average area fraction of the equiaxed α phase, area fraction of lath α phase, total area fraction of α phase, and mean linear intercept of α laths. Stereological analysis of the micrographs was carried out using MIPAR. An image processing routine was created to separate equiaxed α from lath or plate α, as well as to sharpen edges and watershed so that each lath could be represented as a singular microstructural feature. Four stages of the image processing procedure are shown in Figure 8. After the routine was created, sets of micrographs from each heat treated sample were processed and quantified.
The mean linear intercept of $\alpha$ laths and the total area fraction of $\alpha$ phase was determined for both the bimodal and fully lamellar microstructures. It is necessary to point out that a mean linear intercept was reported, instead of the mean $\alpha$ lath width, because the orientation of the $\alpha$ laths does not allow for a direct measurement of their actual thickness. Furthermore, the image processing was carefully done to most accurately capture the mean linear intercepts of $\alpha$ laths, but the routine was designed specifically for images with similar microstructures. As a result, the repeatability of this routine would suffer for microstructures with other features. The fully lamellar microstructure was quantified with a simplified version of the image processing routine.
used on the bimodal microstructure without the need for an equiaxed α identification and subtraction processing step.

2.6 ChemiSTEM™ XEDS

Chemical information from the retained β of a bimodal microstructure was obtained by using ChemiSTEM XEDS on a prepared FIB foil. The small spatial resolution of a thin-film XEDS scan was needed because of the size and distribution of equiaxed α phase. However, as the sample volume and the electron beam size decreases, the number of counts decreases and the statistics of results suffer. Therefore long acquisition times are necessary. ChemiSTEM XEDS utilized four close-proximity windowless silicon drift detectors (SDD) and fast electrons to increase overall counts and drastically reduce analysis time.

2.6.1 K-factor calibration

The accuracy of k-factors calculated from first principles in a system are typically accurate within about ±20%. As a result, experimental k-factors needed to be determined on a standard for a much more accurate composition to be determined [22]. A quantitative XEDS analysis to yield accurate results can only be achieved if a standard of known composition is used to develop k-factors for the specific material. The measured intensities of the elements in the sample can be related to the weight percentages in the sample by the Cliff-Lorimer equation.

\[
\frac{C_A}{C_B} = k_{AB} \frac{I_A}{I_B}
\]  

[1]
We know the concentrations of component A and component B, and we can measure the intensities of component A and component B, but a standard needs to meet several characteristics to be ideal for determining $k_{AB}$ [22]. A single phase, relatively homogenous material is best for using as a standard, so a sample of TIMETAL®18 was $\beta$ solution treated and quenched to room temperature, yielding a microstructure of large retained $\beta$ grains. An FIB foil was removed from the center of one $\beta$ grain.

It is also necessary that the material is capable of being thinned to electron transparency while retaining the same characteristics of the bulk material, without inducing chemical changes [22]. Care was taken to thin the FIB foil with the Ga ion source column in order to minimize the chance for implantation of Ga ions and the potential for redepositing material. In a bulk sample the k-factor is used to take into account effects associated with x-rays. They are the effect of atomic number, $Z$, the absorption of x-rays from surrounding material in the sample, $A$, and the fluorescence of x-rays from within the sample, $F$. But as the sample volume decreases from a large bulk sample to a thinned foil, the interaction volume decreases. At very small volumes the effect of absorption and fluorescence are negligible, and so the k-factor becomes a correction factor for $Z$.

ChemiSTEM XEDS scans were taken from the retained $\beta$ region of the thinned FIB foil. The peak intensities from Ti, Al, Mo, V, Cr and Fe were recorded and the k-factors were determined. The k-factors were then appended to the Esprit software so that the standard k-factors could be used directly to analyze future scans on TIMETAL®18.
samples. The compositions of the retained $\beta$ phase in the two starting microstructures were then used to estimate the $\alpha$ and $\beta$ phase free-energy curves with the use of weighted alloying content equations discussed in Section 2.7. The composition of the retained $\beta$ region of the $\beta$ solution treated condition was determined and used to calculate a Molybdenum Equivalency and Aluminum Equivalency for use in Thermo-Calc calculations for the free energy of formation of the $\alpha$ and $\beta$ phases at various temperatures. The composition of the retained $\beta$ region of the bimodal microstructure was determined and used to calculate a Molybdenum Equivalency and Aluminum Equivalency for use in Thermo-Calc calculations for the free energy of formation of the $\alpha$ and $\beta$ phases at various temperatures. This was used to probe the microstructural refinement expected from a pseudospinodal reaction, as well as the relationship of multi-component alloying content on the ability to understand nucleation pathways in a simplified binary system.

2.7 $\beta$-Stability and Thermo-Calc Calculations

In order to simplify the thermodynamic calculations, the use of aluminum and molybdenum equivalent alloying content equations was implemented so that the calculations are based on the binary Ti-Mo system. The Aluminum Equivalency and Molybdenum Equivalency were used to calculate the overall amount of $\beta$ stability, where weight percent of aluminum alloying content was taken as the equivalent but opposite of the weight percent molybdenum alloying content. The Molybdenum Equivalency, $[Mo]_{EQ}$, was calculated for TIMETAL®18, in which the alloying elements of interest were Mo, V, Cr, and Fe.
\[ [Mo]_{EQ} = [Mo] + 0.2[Ta] + 0.28[Nb] + 0.4[W] + 0.67[V] + 1.25[Cr] + 1.25[Ni] + 1.7[Mn] + 1.7[Co] + 2.5[Fe] \]  \hspace{1cm} [2]

The Aluminum Equivalency, \([Al]_{EQ}\), was calculated for TIMETAL\textsuperscript{®}18, in which the alloying elements of interest were Al, and O.

\[ [Al]_{EQ} = [Al] + 0.17[Zr] + 0.33[Sn] + 10[O] \]  \hspace{1cm} [3]

The overall extent of \(\beta\)-stability, the composition on the Ti-Mo binary diagram, was estimated as the difference between the Molybdenum Equivalency and Aluminum Equivalency.

\[ [TiMo]_{Binary} = [Mo]_{EQ} - [Al]_{EQ} \]  \hspace{1cm} [4]

Once the \(\beta\)-stability, described in weight percent molybdenum, was determined, it was used to calculate the free energy of formation curves at several temperatures. Both \(\alpha\) and \(\beta\) phase curves at various temperatures, starting from just below the processing temperature down to room temperature, were calculated with Thermo-Calc. The pseudospinodal decomposition mechanism of nucleation is based on small compositional fluctuations near the intersection of \(\alpha\) and \(\beta\) free energy curves. It is the proximity of the \(\alpha\) and \(\beta\) curve intersection to the Ti-Mo composition determined in Equation 4 that
enables pseudospinodal decomposition of a homogeneous solid solution of \( \beta \) phase to a fine distribution of \( \alpha \) and \( \beta \) phases.
Chapter 3: Results and Discussion

This study was taken on with two main objectives. The first was to investigate thermal processing by heat treatment of the alloy in two starting conditions and to document the microstructures that were developed in the alloy. The other was to investigate and gain an understanding of the secondary nucleation of $\alpha$ phase in a $\beta$ matrix. This was accomplished by thermal processing above the $\omega + \beta$ and $\beta' + \beta$ phase field. ChemiSTEM XEDS and Thermo-Calc were necessary tools in understanding the composition- and temperature-dependent driving force for nucleation associated with a pseudospinodal decomposition mechanism. The microstructures developed through a number of heat treatments will be shown as a general overview of the morphologies that can be developed in TIMETAL®18.

3.1 Microstructural Evolution in Multiple Processing Routes

In this study, the microstructures developed were centered around typical heat treatments used in industry. Both bimodal and $\beta$ processed microstructures were investigated. The material provided by TIMET was TIMETAL®18 in a bimodal condition. The material was worked at 818°C. It was then quenched to room temperature, to result in a microstructure with dispersed equiaxed $\alpha$, with an average diameter of about 3 µm as shown in Figure 9.
3.1.1 $\beta$ Solution Treated + Quenched to Room Temperature

The recrystallization of the alloy upon solution treating above the $\alpha/\beta$ transformation temperature was necessary to investigate $\beta$ processed microstructures. A number of solution treatment times were investigated to guide the heat treatment schedule for the rest of the heat treatments. It was determined that 15 minutes at 910°C was sufficient for recrystallization. An example of this starting condition can be seen in Figure 10.
3.1.2 β Solution Treated + Quenched to Room Temperature + Aging

In these samples, the starting material was solution treated for 15 minutes at 910°C, then quenched to room temperature and aged at a final aging temperature. Upon quenching to room temperature, the athermal ω phase was nucleated as a distribution of very fine precipitates on the order of a few nanometers. Determining the presence of athermal ω is discussed further in Section 3.3.1. The resultant microstructure from this type of thermal processing is lamellar α in a β matrix. The size and morphology of nucleated α is dependent on the processing temperature, with a decrease in nucleated α phase precipitate size corresponding to a decrease in aging temperature. A very refined microstructure with α laths was nucleated during heat treatment at 500°C, as shown in Figure 11. As the heat treatment temperature is increased, the precipitated α size

Figure 10: 910°C for 15 minutes + quenched to room temperature
increases and the morphology shown in Figure 13 or Figure 14 would be described as plate-like or lamellar $\alpha$.

Figure 11: 910°C + quenched to room temperature + 500°C for 2 hours + quench
Figure 12: 910°C + quenched to room temperature + 600°C for 2 hours + quench

Figure 13: 910°C + quenched to room temperature + 700°C for 2 hours + quench
3.1.3 β Solution Treated + Step Quenched + Aging

In these samples, the starting material was solution treated for 15 minutes at 910°C and then step-quenched directly to the final aging temperature. The samples were not quenched to room temperature and the aging temperatures were above the upper limit of ω stability. The resultant microstructure from this type of thermal processing is lamellar α in a β matrix, just as in the case of the samples quenched to room temperature and then aged. The size and morphology of nucleated α is dependent on the processing temperature, with a decrease in nucleated α phase precipitate size corresponding to a decrease in aging temperature. A relatively refined microstructure with α laths was nucleated during heat treatment at 600°C, as shown in Figure 15. As the heat treatment
temperature is increased, the precipitated α size increases and the morphology shown in Figure 16 would be described as plate-like or lamellar α.

Figure 15: 910°C + step-quenched to 600°C for 2 hours + quench
Figure 16: 910°C + step-quenched to 700°C for 2 hours + quench

Figure 17: 910°C + step-quenched to 800°C for 2 hours + quench
3.1.4 \( a/\beta \) Solution Treated + Quenched to Room Temperature + Aging

In these samples, the starting material was worked at 810\(^\circ\)C quenched to room temperature. The samples were then heat treated at various aging temperatures in the \( \alpha + \beta \) phase field. The resultant microstructure from this type of thermal processing is lamellar \( \alpha \) and equiaxed \( \alpha \) in a \( \beta \) matrix. This is the bimodal microstructure. The size of the equiaxed \( \alpha \) phase is a function of the amount of work done, the temperature at which it was done, and the cooling rate from processing temperature. The size and morphology of \( \alpha \) nucleated during the aging treatment is dependent on the processing temperature, with a decrease in nucleated \( \alpha \) phase precipitate size corresponding to a decrease in aging temperature.
Figure 18: As-received material + 500°C for 2 hours + quench
Figure 19: As-received material + 600°C for 2 hours + quench

Figure 20: As-received material + 700°C for 2 hours + quench
3.2 Microstructural Quantification

The mean linear intercept and total volume fraction of $\alpha$ phase were determined for the fully lamellar and bimodal microstructures that were quenched to room temperature and then heated to aging temperatures. In both microstructures, the mean linear intercept of $\alpha$ laths decreased with decreasing temperature as expected. The mean linear intercept of the bimodal microstructure was much less than that of the fully lamellar microstructure for higher temperatures. As the aging temperature decreases, it seems that the mean linear intercept of both microstructures decreases until similar values of both are measured at the aging temperature of 500°C as shown in Figure 22. The volume fraction of $\alpha$ phase that is precipitated increases with decreasing temperature, except for the decrease seen in the bimodal microstructure heated at 500°C. This
highlights some of the issues with using similar stereological procedures to determine the size and quantity of microstructural features that differ in size by an order of magnitude. The volume fraction of α phase precipitated in the 500°C heat treatment may have been less than the 600°C heat treatment, but may also be attributed to difficulty in resolving and accurately measuring the very thin α laths precipitated at 500°C.

Figure 22: Mean linear intercept of the quenched to room temperature + aged samples
3.3 Pathways for α Phase Nucleation

Because TIMETAL® 18 is a new metastable β alloy, it was necessary to β solution treat a sample and quench to room temperature in order to make sure that α nucleation was suppressed, as well as to see if athermal ω was precipitated. Upon quenching, the resulting microstructure is retained β without the presence of nucleated α. The athermal ω phase was present in quenched samples. This will be discussed in Section 3.3.1 which describes the presence of this metastable phase. The pseudospinodal decomposition mechanism was also investigated as it relates to α phase precipitation in step quenched samples.
3.3.1 Presence of Athermal $\omega$

Diffraction patterns were used to determine the presence of $\omega$ phase precipitates, and dark field imaging was used to view $\omega$ precipitates that had been coarsened by heat treatment at 300°C for 8 hours. The diffraction pattern from a $\beta$ solution treated and quenched sample can be seen in Figure 24. The diffuse reflections can be seen from the presence of very small $\omega$ precipitates.

![Figure 24: [110] diffraction pattern with $\omega$ satellite reflections](image)

A $\beta$ solution treated and quenched sample was then heat treated at 300°C for 8 hours in order to coarsen the $\omega$ precipitates so that they would be more easily captured with dark field imaging. After 8 hours of coarsening, the precipitates were still less than 10 nm in size on average. They can be seen in Figure 25.
3.3.2 Pseudospinodal Nucleation

Heat treatments that incorporate a quench to room temperature nucleate small, coherent precipitates. A nucleation pathway that includes quenching to room temperature will therefore have some interaction with these precipitates. Heat treatments above the ω phase field were used to examine the nucleation of α phase precipitates and to probe the mechanism that causes the $\beta \rightarrow \alpha$ reaction. A pseudospinodal decomposition mechanism would take place at a specific temperature where the free energy curves are close enough that small compositional fluctuations could cause nucleation. This mechanism is dependent on local composition and temperature. Therefore, the pseudospinodal
temperature is alloy dependent and also dependent on the starting microstructure of the alloy. The retained β phase in the β solution treated and quenched sample is expected to be very close to the alloy chemistry. When the starting condition is bimodal, the alloy has had time for nucleation and growth of equiaxed α phase. The nucleation of the α phase should result in the consumption of α-stabilizers, as well as the rejection of β-stabilizers and therefore cause an increase in the β stability of the β retained region. Developing an understanding of the nucleation reaction associated with this mechanism and being able to estimate the pseudospinodal temperature based on alloy composition could be useful in alloy design.

3.4 Developing k-factors and Determining Retained β Composition

A standard sample of known composition was used to calculate the k-factors for TIMETAL® 18 in the ChemiSTEM XEDS system. With the known composition and measured peak ratios the k-factors were determined numerically in the Esprit software to satisfy the sum of all elements being equal to 100%. Using equations for the Molybdenum Equivalency and Aluminum Equivalency, the general α-stability and β-stability were calculated from the determined compositions.
The over β-stability was higher in the retained β region of the bimodal microstructure. It is interesting to point out that the retained β region showed an increase in all β-stabilizing elements to differing degrees, but only a slight amount of decrease in the α-stabilizer content. With the retained β region of the bimodal microstructure more heavily β stabilized than the retained β region of the β processed microstructure, a difference in the pseudospinodal temperature would be expected. In Section 2.7 the β-stability was described in terms of the composition on the Ti-Mo binary phase diagram. In Table 3 we can see that the point on the Ti-Mo binary phase diagram would shift from 6.93 wt% to 9.79 wt% for the retained β region of the bimodal microstructure. Because the pseudospinodal decomposition mechanism relies on the proximity of the α and β free energy curves to the composition of interest, the temperature for a more heavily β stabilized composition would be lower.
3.5 Thermo-Calc Free Energy Calculations

Using the $\beta$-stability of the retained $\beta$ of both starting microstructures, the pseudospinodal temperature could be calculated based on the Ti-Mo phase diagram. The free energy curves of the $\alpha$ phase and $\beta$ phase are plotted at a given temperature. The intersection of the two curves represents the composition necessary for a pseudospinodal decomposition reaction. Thermo-Calc software was used to calculate free energy curves for the bimodal and standard compositions at 6.93 and 9.79 wt% Mo, respectively. The temperature was varied until the free energy curves had an intersection within 0.2 wt% Mo of the calculated $\beta$ stabilities.

![Figure 26: Calculated $\alpha$ and $\beta$ phase free energy curves at 640°C](image-url)
Figure 27: Calculated $\alpha$ and $\beta$ phase free energy curves at 590°C

The free energy curves intersect near 6.93 wt% Mo at 640°C, as shown in Figure 26. From this estimate, the pseudospinodal decomposition mechanism would be expected to occur for the $\beta$ processed or fully lamellar microstructure near 640°C. The free energy curves intersect near 9.79 wt% Mo at 590°C, as shown in Figure 27. From this estimate, the pseudospinodal decomposition mechanism would be expected to occur for the bimodal microstructure near 590°C. Using Thermo-Calc calculations at several temperatures and the $\beta$-stability of each condition, it would be expected that, starting with a bimodal microstructure with a more $\beta$ stabilized retained $\beta$ region, the pseudospinodal decomposition mechanism would be suppressed about 50°C. This was tested experimentally by solution treating at 910° and 810°C for the $\beta$ processed and bimodal starting microstructures, respectively, followed by aging at the final aging temperature.
3.6 Step Quenching Heat Treatments Near Pseudospinodal Temperature

Examination of the microstructures shown in Section 3.1.2, Section 3.1.3, and Section 3.1.4 was used to determine the temperature range where refinement takes place in each starting condition microstructure. In both the starting conditions, the resulting microstructures indicated that a refinement was taking place between 600 – 700°C. Although the microstructural refinement followed a general trend with respect to final aging temperature the 600 – 700°C, temperature range seemed to encompass a transition from larger plate like \( \alpha \) to a much more refined lath \( \alpha \) microstructure.

3.6.1 Fully Lamellar Step Quenched Heat Treatments

The microstructural refinement that takes place because of pseudospinodal decomposition in the \( \beta \) processed fully lamellar microstructure takes place near 610°C, as shown in Figure 28 through Figure 33.

Figure 28: 910°C + step quenched to 650°C for 2 hours + quench
Figure 29: 910°C + step quenched to 640°C for 2 hours + quench

Figure 30: 910°C + step quenched to 630°C for 2 hours + quench
Figure 31: 910°C + step quenched to 620°C for 2 hours + quench

Figure 32: 910°C + step quenched to 610°C for 2 hours + quench
The refinement in microstructure can be seen in comparing Figure 31 and Figure 32. The microstructural features developed in each heat treatment were measured. The mean linear intercept of the α laths can be seen in Figure 34. The quantified mean linear intercepts are somewhat less demonstrative than viewing the microstructures. The mean linear intercept of the α laths in the 600°C quenched-to-room-temperature sample was 235 nm, as shown in Figure 22, and the mean linear intercept of the step-quenched sample was 342 nm. This indicates that, although a definite refinement in microstructure exists for step-quenched samples aged below a certain temperature, it seems that quenching to room temperature may result in a slightly more refined microstructure at the same aging temperature. This may indicate that quenching to room temperature does produce precursors that may be athermal ω or misfit dislocations produced from thermal stresses during quenching. The step-quenched samples still precipitated a refined
homogenous distribution of $\alpha$ laths without utilizing precursors formed during quenching to room temperature. Pseudospinodal decomposition may still explain this phenomenon, and examining the effect of composition on the precipitation of $\alpha$ in metastable $\beta$ alloys will help gain an understanding of this mechanism.

![Graph showing mean linear intercept of $\alpha$ laths in fully lamellar microstructures](image)

**Figure 34:** Mean linear intercept of $\alpha$ laths in fully lamellar microstructures

### 3.6.2 Bimodal Step Quenched Heat Treatments

The pseudospinodal refinement takes place over a short temperature range and this can be seen in the fully lamellar microstructure. The refinement that takes place in the bimodal microstructure was less distinct. The images shown will be in 20°C increments.
Figure 35: 810°C + step quenched to 650°C for 2 hours + quench

Figure 36: 810°C + step quenched to 630°C for 2 hours + quench
Figure 37: 810°C + step quenched to 610°C for 2 hours + quench

Figure 38: 810°C + step quenched to 590°C for 2 hours + quench
The microstructural refinement that takes place because of pseudospinodal decomposition in the bimodal microstructure takes place near 590°C, as shown Figure 35 through Figure 38. It appears that the higher β stability of the retained β region in bimodal microstructure suppresses this type of nucleation mechanism about 20°C in TIMETAL®18. The mean linear intercept of the α laths can be seen in Figure 39. Again, the quantified mean linear intercepts are somewhat less demonstrative than viewing the microstructures. The mean linear intercept of the α laths in the 600°C quenched-to-room-temperature sample was 103 nm, as shown in Figure 22, and the mean linear intercept of the step-quenched sample was 278 nm. This indicates that, above the pseudospinodal temperature of 590°C, it seems that quenching to room temperature has a more definitive affect on the refined the microstructure. The measured mean linear intercepts for all of the bimodal microstructures were lower than the mean linear intercepts of the fully lamellar microstructure, which was also seen in the quenched-to-room-temperature samples.
3.7 Mechanical Properties Near Pseudospinodal Temperature

The Vickers hardness of each of the heat treatments from both the bimodal and β processed microstructures was measured. The hardness of the β processed samples can be seen in Figure 40 and the bimodal samples can be seen in Figure 41. Very similar hardness values are obtained for both microstructure heat treated between 630 - 650°C, but the fully lamellar samples increase in hardness more rapidly with decreasing temperature below 630°C. No abrupt increase in hardness was seen in the hardness values of the β processed samples but a somewhat abrupt increase in hardness was seen in the bimodal microstructure from 610 to 600°C.

Figure 39: Mean linear intercept of α laths in bimodal microstructures
Figure 40: Vickers hardness of fully lamellar microstructures

Figure 41: Vickers hardness of bimodal microstructures
A large variation in \( \alpha \) phase morphology and the overall microstructure can be achieved through different processing routes. The final heat treatment stage in both the \( \beta \)-processed (fully lamellar) and \( \alpha/\beta \) processed (bimodal) microstructure is responsible for the development of secondary \( \alpha \) lath morphology. The mean linear intercept of the \( \alpha \) laths produced during this heat treatment increases with decreasing heat treatment temperature. The mean linear intercepts of the laths produced in the bimodal microstructure are smaller than the mean linear intercept of the laths in the fully lamellar microstructure at elevated temperatures, but heat treatment temperatures near 500°C produce similarly size \( \alpha \) laths. The more refined \( \alpha \) lath microstructure in the bimodal condition may be caused by a higher dislocation content, associated with working at 810°C, in the retained \( \beta \) phase, or may be a product of growth limitations because of the close proximity distribution of small equiaxed \( \alpha \) phase particles.

In the literature there is some discussion on the effect of \( \omega \) phase precipitates on the precipitation of homogenously distributed \( \alpha \) phase microstructures. Processing routes that started from well above the upper limit of \( \omega \) phase stability and step quenched to aging temperatures also above the upper limit of \( \omega \) phase stability yielded homogeneously distributed \( \alpha \) phase. It is proposed that the mechanism associated with this transformation is a pseudospinodal decomposition mechanism by which the \( \beta \) phase decomposes to the \( \alpha \) and \( \beta \) phase. The pseudospinodal transformation involves the decomposition of a homogeneous parent phase into two subsequent phases that continuously change in composition until reaching their equilibrium compositions. Heat
treatments that did and did not incorporate the $\alpha$ phase in the transformations showed that, although precursors are not necessary for precipitating homogeneous distributions of $\alpha$ phase, they may have a small affect on precipitating refined microstructures.

A method to determine the overall $\beta$-stability of multi-component metastable $\beta$ titanium alloys was used in concert with Thermo-Calc to determine the temperature at which pseudospinodal decomposition may take place. The $\beta$-stability of the retained $\beta$ region of $\beta$-processed and $\alpha/\beta$ processed was determined by wet chemistry and XEDS, respectively. The $\beta$-stability of retained $\beta$ was taken as the difference between the Molybdenum Equivalency and Aluminum Equivalency and reported in terms of weight percent molybdenum on the Ti-Mo binary phase diagram. Thermo-Calc was then used to calculate the free energy of the $\alpha$ and $\beta$ phase in the Ti-Mo binary system at various temperatures. The estimated temperature at which the pseudospinodal decomposition mechanism was expected to occur were 640°C and 590°C for the $\beta$-processed and $\alpha/\beta$ processed starting microstructures, respectively. The experimentally determined temperatures at which the pseudospinodal decomposition mechanism were 610°C and 590°C for the $\beta$-processed and $\alpha/\beta$ processed starting microstructures, respectively. The temperature at which pseudospinodal decomposition is expected to occur in multi-component alloys can only be estimated with the use of alloying content equivalencies. The experimental and calculated results showed good agreement, but the ability to calculate free energy curves taking into account the interaction of multiple alloying elements is necessary.
The methods used here can help to evidence the pseudospinodal decomposition of \( \beta \) to \( \alpha \) and \( \beta \) in TIMETAL\textsuperscript{®}18, but the use of more in-depth determinations of free energy are necessary in the future to accurately predict this type of transformation. This work focused on the phase transformations and microstructure development of a metastable titanium alloy. Similar microstructures can be achieved through \( \omega \)-influenced and \( \omega \)-free phase transformation pathways. In future work, the mechanical properties of these two types of processing routes need to be examined.
References

1. Lütjering, G., Williams, J.C., Titanium. 2nd ed. 2007: Springer 442.


