Development and Application of Advanced Electron Microscopy Characterization Techniques to Binary Titanium – Molybdenum Alloys

Dissertation

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Abstract

The direct three-dimensional characterization and visualization of structural materials using characterization techniques such as the DualBeam™ Focused Ion Beam (DB-FIB) instrument has resulted in a significant increase in the level of understanding of materials microstructures. Indeed, visualizations of three-dimensional datasets can provide directly interpretable results (both quantitatively and qualitatively) regarding the true morphology and distribution of phases. This thesis, in part, develops a methodology and examines the accuracy of the quantitative measurements and the clarity of the qualitative descriptions afforded by the application of the DualBeam™ FIB as a tool for the three-dimensional characterization of Ti-based alloys.

The Dual Beam™ FIB systems also provide a method for site-specific TEM sample preparation which greatly reduced the amount of time necessary to isolate desired features. This method creates relatively significant damage during the sputtering process and subsequently hinders further analysis and in some cases prevents further analysis. A methodology for predictive, low – energy ion milling technique for optimal HR-STEM
and HR-TEM sample preparation is developed in conjunction with the Fischione NanoMill™.

The methodologies developed in this work have been applied to binary Ti-Mo alloys to prove their validity. β-Ti alloys exhibit several complex and competing phase transformations such as nucleation of the metastable omega-phase at low to intermediate temperatures and β-phase separation at intermediate temperatures. Both omega-phase and/or beta-phase separation have been proposed as heterogeneous sites assisting in intragranular nucleation and growth of the α-phase.

Through studying the commercial alloy the model binary Ti-Mo system, an attempt is made to understand the stability of the ω-phase and factors governing the nucleation of the α-phase at low to intermediate temperatures. For the first time, using a combination of HR-STEM, HR-TEM, and 3DAP tomography the structure and composition of the omega phase, as well as the alpha/beta, omega/beta interfaces are investigated for various thermal histories.
Dedication

This document is dedicated in memory of the most significant person to my life, my
Mother.
Acknowledgments

Words cannot express, nor can I convey the necessary acknowledgement of all the people who have contributed to my completion of this document as well as my maturation as an individual and researcher. None of this would have been possible however, without my Lord and Savior.

“I can do all things, through Christ who strengthens me.” Philippians 4:13

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Perhaps one of the most educational aspects of working with Dr. Fraser, is the opportunity to have some of the best minds in their respective fields come and work with you. This process has been invaluable and I must thank all of the visiting scientists I have had the opportunity to learn with. A special thanks is extended to Dr. Dennis Maher and Dr. Andrew Johnson, your knowledge and expertise of TEM and characterization have allowed me to explore features I never thought possible.

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A special thanks is extended to my grandparents, Ivy and Mary, as well as Felder and Gladys. These four people helped shape my life more than most and took integral parts in my life, without them I would not be the person I am today. I was able to see first hand the importance of hard work and perseverance, in life as well as marriage. I could not have had better examples for a happy life.

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involved parent. I hope that you realize the completion of this work is a direct reflection on the values instilled from you.

Lastly, and probably most importantly, I have to thank the lady who has taken away every other concern in the world and allowed me the time to finish this document so that we may enjoy our future lives together. Amy, I didn’t start this endeavor for you, but I certainly finished it for our lives together.
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CHAPTER 1

Introduction

Traditional titanium alloy development has been based on the premise that microstructure controls properties and that processing controls microstructure, hence; design methodologies have involved experimental determination of interrelationships between these three parameters. Recently, in response to the necessity to reduce time and costs for development of new materials and optimization of existing ones; concerted efforts have been directed towards optimizing these parameters through a computational approach such that interrelationships may be predicted and subsequently, developed into design tools.

Multiple obstacles hinder the development and implementation of such predictive tools and must be overcome in order for productive implementation by both materials engineers and component designers. First, hindering this endeavor has been the representation of microstructures as average numerical values to facilitate incorporation into computational models. Titanium microstructure, as well as generic material
microstructure, has complex, interdependent morphologies and therefore comprehensive characterization has, in the past, eluded materials scientists.

To assist in this area, computational models have developed using average values of microstructural features determined, more or less, robustly on the basis of stereological procedures performed on two-dimensional images. The inability of stereology to characterize spatially varying aspects of microstructures in real engineering alloys has resulted in models exhibiting low-fidelity and poor accuracy. Quantification methods for characterizing microstructural features must be developed.

Second, many predicative models involve computationally intensive methods, such as phase-field modeling and finite element modeling. No reasonable database exists to readily generate input variables into these models and current methods require empirical, stereological measures. It is unrealistic to develop design tools that involve lengthy periods of computation using super computers or clusters as well as exorbitant man-hours to compile input. A method for incorporating this quantitative information into a format useable by modelers would be extremely beneficial to the field, along with the refinement of our stereological procedures for better prediction by the neural networks.

Third, collection of quantitative data is not trivial. The microstructure found in titanium based alloy systems is very complex and hence traditional one-point correlation functions (such as volume fraction and average particle size) are not sufficient to quantitatively define microstructure; nor do they allow for establishing robust
microstructure property relationships. The straightforward, intimate coupling between precipitate morphology and spatial distribution clearly reveals the limitation of such poor descriptors, as three-dimensional analysis can characterize uniquely spatial distribution and morphology. Therefore, one of the primary objectives of this thesis is to develop a novel methodology for collecting high fidelity, three dimensional, serial section data sets from titanium based alloys using a commercially available, dual-beam focused ion beam/scanning electron microscope (DB-FIB/SEM).

The dual beam FIB/SEM is a combination of scanning electron microscope as well as a scanning focused ion beam. The combination of both electron and ion imaging optics, along with the ability to specifically mill local regions of interest; has created a new world of possibilities for characterizing engineering alloys. One such possibility afforded by the DB-FIB/SEM is automated milling and image collection to form a serial section interrogation of a given volume. Upon undertaking this thesis endeavor, very minimal work had been performed with a single beam FIB to crudely remove and image successive layers. The inception of the DB-FIB, however, created an opportunity to develop a methodology to produce high-fidelity, serial-section data sets as well as generate site-specific transmission electron microscopy (TEM) samples and three-dimensional atom probe (3DAP) samples.

The challenge in preparing TEM samples is to create specimens that are electron transparent, while also possessing negligible surface damage and roughness. The presence of any surface artifact convolutes the transmitted signal and makes both the
interpretation of the image and chemical analysis cumbersome, if not impossible. It is well known that ion milling artifacts readily form upon ion bombardment and therefore, any FIB milled TEM sample will contain a surface layer encapsulating the undamaged specimen. However, despite significant advances in transmission electron microscopy, such as implementation of aberration correction and source monochromation, to improve resolution and characterization performance; sample preparation is still one of the most crucial steps in determining the quality and precision of results obtained from analytical TEM characterization techniques. Along with better TEM resolution comes an even more critical need for damage free specimens. Also possible is the ability to characterize ion-induced damage to a level never before achieved and in turn refine FIB-based TEM sample preparation.

Along these lines, this thesis is divided into six chapters pertaining to the methodology and development of the DB-FIB/SEM as a tool for advanced electron microscopy characterization as well as application of these methods to titanium based alloys.

Chapter Two is an introduction to a few topics to give the reader an overview of microstructure-property relationships, as well as traditional ways of characterizing these features. Basic titanium alloys information, along with pertinent phases and phase transformations is provided as motivation for application of methodologies developed in Chapter Four. Basic image processing and three-dimensional analysis from serial section
data is also discussed. Lastly, some brief background and technical analysis of electron microscopy equipment and techniques is presented.

Chapter Three is a description of experimental methods employed throughout the work presented in this thesis as well as descriptions of various analytical and characterization tools utilized for this work. This joins nicely with Chapter Four in which two methodologies are developed with the DB-FIB/SEM to characterize uniquely titanium-based microstructures.

Chapter Five presents the first visualization and application of three-dimensional serial section collection and analysis using a DB-FIB/SEM to Widmanstätten alpha growth from allotriomorphic grain boundary alpha. This analysis is combined with electron backscattered electron diffraction (EBSD) to provide a powerful coupling of crystallographic information along with morphological information.

Chapter Six utilizes a combination of 3DAP and aberration corrected TEM to characterize omega phase in binary Ti – 18 wt% Mo at the nanometer level. Experiment evidence for the formation and growth of omega precipitates is validated for the first time through high-resolution TEM and accurate compositional analysis is also presented from 3DAP analysis. Furthermore, the three-dimensional morphology of omega has been shown for the first time. The novelty of this work lies in that it was only made possible by low-energy ion milling techniques developed in Chapter Four. Indeed, without the proper sample preparation and damage reduction; analytical, high-resolution TEM can prove impossible and all TEM analysis is improved by low energy ion milling.
Chapter 2

Background and Literature Review

2.1 Introduction

Titanium alloys are currently one of the most widely used groups of materials for industrial, medical, and domestic applications. The initial stimulus for development came from the aerospace industry, where a need for materials that possess high strength to weight ratio at elevated temperatures is desired. More recently, the importance of the alloys as a corrosion resistant material has been recognized by the medical field for use as biocompatible implants in the human body[1]. Titanium alloys have been intensely studied over the last few decades due to these important technological applications. The microstructure of two-phase $\alpha/\beta$ titanium alloys is very complex and strongly dependent on processing and thermo-mechanical history. In order to better understand and predict the properties of titanium alloys, phenomenological quantification and modeling are necessary. The ability to optimize microstructure, and thus optimize alloy properties,
requires an understanding of the influence different microstructural parameters have on mechanical properties. Analogously, in order to understand the complex morphological features present in titanium alloys, a three dimensional, quantitative understanding and representation of critical features must be developed.

2.2 Phases in Titanium Alloys

Titanium is an allotropic element; existing in more than one crystallographic form.[2-6], Titanium has a hexagonal close-packed (hcp) crystal structure at low temperatures with two Ti atoms at (0,0,0) and (1/3, 2/3, 1/2). Fig 1(a) This phase is referred to as alpha titanium. The alpha phase transforms to a body centered cubic (bcc) phase upon heating above 883 °C (1621 °F) in pure titanium. The bcc phase is referred to as beta titanium and Ti atoms are located at (0,0,0) and (1/2, 1/2, 1/2). Fig 1(b) Titanium also forms two equilibrium intermetallic phases that are of significance, Ti₃Al and TiAl. Ti₃Al(α₂) is formed in alloys containing more that 6 wt% Al and this reaction is promoted by higher oxygen content. TiAl(γ) can be observed in Ti alloys having high Al content.

There are three non-equilibrium phases, hexagonal martensite (α’), orthorhombic martensite (α”), and omega (ω) that also occur in Ti alloys[2, 4]. α’ is a supersaturated alpha phase having a fine lath morphology produced by diffusionless transformation of beta upon rapid cooling from the beta phase. It is more readily formed in α/β alloys that have low amounts of beta stabilizing elements because the Mₛ temperature decreases with increasing beta stabilizing elements. Morphologically, it is very similar to equilibrium
alpha, although it is usually more well-defined and thinner with straight edges. $\alpha'$ is also produced by a diffusionless transformation and there is confusion in the literature with respect to nomenclature[2, 7]. Omega is a submicron, hexagonal phase and is proposed as a transition phase during the formation of alpha from beta[2, 5-9]. It is found in alloys with large beta stabilizing elements and leads to embrittlement. Omega can form within the beta matrix if certain compositions during quenching are present, as an isothermal transformation product, as a precipitate during ageing, or by high hydrostatic pressures[2].

2.3 Titanium Alloy Classification and Effect of Stabilizing Elements

2.3.1 Alpha Stabilized Ti – Alloys

Unalloyed titanium and alloys of titanium containing alpha stabilizers are hcp at room temperature and classified as alpha alloys. Moderate strength, toughness, creep resistance, and weldability characterize these alloys. Alpha alloys are also suitable for cryogenic applications due to the absence of a ductile to brittle transition. Alpha stabilizing elements are listed in Table 1 and can be further subdivided into two categories. Pure alpha stabilizers, such as substitutional aluminum, gallium, germanium and interstitial oxygen, elevate the temperature of the beta transus as a function of composition, which stabilizes the formation the alpha phase. Fig 2(a) Alpha
strengthening elements, such as tin and zirconium, have a high solubility in the alpha phase and act as solid solution strengtheners.

A practical limit exists as to the amount of alpha stabilizing elements that may be added to titanium since the alloys tend to embrittle if the aluminum equivalent exceeds approximately 9 %[6]. This quantity can be calculated with Equation 1.

\[
[Al]_{eq} = [Al] + \frac{[Zr]}{6} + \frac{[Sn]}{6} + 10[O + C + 2N] \quad \text{Equation 1}
\]

Alpha alloys cannot be strengthened by heat treatment because the alpha phase is stable. The only ways to strengthen alpha alloys is cold work, cold work followed by annealing to control alpha grain size, or solution strengthening. Alpha alloys that contain 1-2% beta stabilizers have been classified as near-alpha alloys and can exhibit microstructural changes similar to that in α/β alloys, however, do not respond well to heat treatment or aging.

2.3.2 Beta Stabilized Ti – Alloys

Beta alloys are formed with large amounts of beta stabilizers that are generally transition metals that stabilize the bcc phase. Beta stabilizing elements can be divided into two groups, beta isomorphous and beta eutectoid stabilizers. Beta isomorphous additions such as vanadium and molybdenum continuously lower the beta transus temperature with increasing concentration[2]. Fig 2(b) There are also beta eutectoid
stabilizers such as iron and chromium which lower the beta transus until the process is interrupted by a compound formation. Fig 2(c) Beta alloys have excellent forming characteristics due to the retained bcc phase, relatively low strength and good toughness. These alloys are also characterized by high hardenability but are unsuitable for elevated temperature applications without prior stabilization or overaging. Hardenability of a titanium alloy refers to its ability to permit full transformation of the alloy to transformed beta or to retain beta to room temperature[1].

The strength of beta stabilizing elements can be gauged by the rate at which they lower the martensite transus and hence the degree to which they permit the retention of the β phase at room temperature without the formation of martensite. The molybdenum equivalence is analogous to the aluminum equivalence in alpha alloys[6]. (Eqn. 2).

\[
[Mo]_{eq} = [Mo] + \frac{[Ta]}{5} + \frac{[Nb]}{3.6} + \frac{[W]}{2.5} + \frac{[V]}{1.5} + 1.25[Cr] + 1.25[Ni] + 1.7[Mn] + 1.7[Co] + 2.5[Fe]
\]

Equation 2

2.3.3 Titanium Alloy Classification

Using the molybdenum and aluminum equivalence equations provides a basis for placement of US technical alloys mapped onto a pseudobinary β-isomorphous phase diagram in Figure 3.
Titanium alloys that contain a mixture of alpha and beta phases in equilibrium at room temperature are known as $\alpha+\beta$ alloys. These alloys combine the strength of alpha alloys with the ductility of beta alloys, and their microstructure and properties can be widely varied depending on heat treatment and/or thermomechanical history. Most alloys contain elements to stabilize and strengthen the alpha phase, together with 4-6% of beta stabilizing elements, which allows 10-50% of the beta phase to be retained on quenching from the ageing temp. $\alpha+\beta$ alloys have the greatest commercial importance and are usually produced in some form of a forged component[1].

2.4 Thermo-mechanical Processing and Microstructural Evolution

A variety of microstructures may be developed in $\alpha+\beta$ alloys by various kinds of heat treatments. The origin of heat treating responses in titanium alloys to solution treatments and aging lies in the instability of the high temperature beta phase at lower temperatures. While grain shape and size affect behavior, the crystal structure changes that occur during processing play the major role in defining titanium properties. Grain refinement, therefore, cannot be obtained by heat treatment, and after one beta to $\alpha+\beta$ sequence is performed, additional cycles have no effect on the basic crystallographic texture, although the structure may be coarsened as a consequence of beta grain growth. Microstructural control is affected by using the proper combination of hot work and heat treatment. Maximum strength levels are achieved in titanium alloys by solution
annealing followed by aging[10]. A wide range of strength levels can be obtained in alpha/beta or beta alloys by these processes as shown in Figure 4.

In general, when an \(\alpha+\beta\) alloy is heated to a temperature above the beta transus, the whole sample is transformed to beta. If the alloy is kept at this temperature for an extended period of time or taken too high above the transus, there may be excessive grain growth in beta, which is to be avoided. Cooling down from the solutionizing temperature to room temperature will give different kinds of microstructure due to the beta to alpha transformation. This transformation can occur by nucleation and growth or it can occur martensitically, depending upon the alloy composition and cooling rate. The effect of cooling rate on the constitution of an \(\alpha/\beta\) alloy is shown schematically in the continuous cooling transformation (CCT) diagram shown in Figure 5.

The \(\alpha'\) structure consists of an acicular hcp martensite, which is supersaturated in \(\beta\) -stabilizing elements such as V or Mo. The nucleation and growth structure consists of colonies of alpha laths, which are separated by thinner laths of \(\beta\) phase. The martensitic structure is always finer and the individual plates are more randomly oriented in comparison with nucleation and growth structure. Low cooling rates will yield a coarse, colony microstructure with alpha heterogeneously nucleating at the prior beta grain boundaries. The thickness and continuity of this layer depends on cooling rate and alloy composition.

In general, as the cooling rate become higher, the lamellae are finer and microstructure may change from colony to Widmanstätten or basket-weave structure. At
very high cooling rates the beta phase is transformed to martensite if the temperature goes below the Ms temperature. Increasing beta stabilizing solute content decreases the Ms temperature and the critical cooling rate above which the Ms temperature becomes independent of cooling rate also decreases. The critical cooling rate needed for a martensitic transformation also decreases with increasing beta stabilizing content[6, 11]. If the alloy is held for an extended period of time in the α+β region, there will be more beta at that temperature, which on cooling would give more transformed beta containing beta and secondary alpha. If the alloy is held at lower temperatures more “equiaxed” or primary alpha is expected.

Thermo-mechanical processing can also play a large role in the microstructural evolution in α+β alloys. If an α+β alloy is forged in the α+β phase field, and then annealed below the beta transus, the alpha phase may undergo recrystallization and globularization depending on the amount of deformation. Globularization is proposed to occur by two different mechanisms[12]. The first involves the pinching off of the α phase by the β phase at the interface between two adjacent recrystallized α crystals and the neighboring β lath. The β phase penetrates the boundary between the two recrystallized alpha grains and in order to reduce the surface tension eventually separates them. The second mechanism involves regions of intense shear bands within the α laths, which again form an α/α interface in contact with a β lath. Again surface tension causes a curvature in the α/β interface and the β phase penetrates the boundary between the two sides of the α crystal across the shear bands and separates them in two crystals. In
general, the alpha will be recrystallized and globularized more the greater the amount of deformation[10, 12]. The recrystallization temperature and cooling rate also affect the final microstructure. In general, the higher the recrystallization temperature, the smaller the fraction of recrystallized, equiaxed $\alpha$, and greater the amount of transformed $\beta$. Similarly, the lower the cooling rate from the recrystallization temperature, the more will the equiaxed $\alpha$ grains grow at the cost of the $\alpha$ lamellae.

### 2.5 Microstructure/Property Relationships

#### 2.5.1 Introduction

Researchers have traditionally characterized microstructural morphologies by conventional optical or electron microscopy and these images are essentially planar representations of the three dimensional structure. Stereology is the science of the geometrical relationships between a structure that exists in three dimension and the images of that structure that are fundamentally two dimensions [14]. Optical and SEM images are restricted to observations of a single plane of polish, while transmission electron microscopy is limited to thin foils of approximately 100 nm of material. Even though stereological techniques can be used for rapidly characterizing the “average value” of many microstructural features, simple three-dimensional shapes often cannot be deduced from examination of random planes of polish, much less the complex
morphologies and distributions of grains and precipitates found in many materials [15]. Also, in order to optimize stereological measurements and analysis for accurate quantification, the three dimensional nature of the features being estimated are necessary. The shapes of many simple features, in known prior to analysis, can be accurately deduced through stereology, however, the sizes, spatial distributions, shapes, and interconnectivities of complex microstructural features can only be characterized with three dimensional analysis [16]. Significant effort has been devoted to determining the morphologies and connectivities of precipitates in many systems through the use of stereology; and more recently in conjunction with artificial neural networks to deduce phenomenological models in Ti alloys [15, 17, 18].

2.5.2 3-D Characterization

The three-dimensional nature of microstructural features, particularly precipitate shape, plays an essential role in the present understanding of microstructural evolution and phenomenological modeling. For example, predictive growth models of grain boundary precipitates [19, 20] and Widmanstätten precipitates [21, 22], along with current phase field modeling [23] depend upon assumed or deduced three-dimensional morphologies of precipitates. The influence of precipitate shape on mechanical properties is also well established [24]. For example, elongated plate or needle-shaped ferrite precipitates can be deleterious to fatigue strength and fracture toughness [25]. No matter
what phenomenon, morphology, or characteristic is modeled, physical or experimental evidence is always needed for validation of the model.

Over the last 40 years dramatic improvements in three dimensional reconstruction and analysis have occurred. In 1962, Hillert [26] and Lange produced a motion picture of serial sections to show the true three dimensional structure of an entire pearlite colony. Eichen et al. [27] studied the growth of Widmanstätten ferrite by measuring the changing length of plates with increasing depth through serial sections. Hawbolt and Brown [28] used serial sectioning to study the shapes of grain boundary precipitates in an Ag-Al alloy. Barrett and Yust [29] showed the interconnectivity of voids in a sintered copper powder. Ziolkowski [30] used a microtome to perform a serial sectioning study of grain boundary precipitates in an alpha/beta brass alloy[31].

In 1976, Rhines et al. [32] discussed the issues regarding serial sectioning analysis. He recommended using a magnification sufficient to show several grains simultaneously and sectioning to a depth of about twice the span of the largest grain in about 250 sections. This rule of thumb must take into account the scale of the features being studied and the limitations of the material removal technique being used. The resolution of the final three dimensional representations in every serial sectioning project to date has been limited by the thickness of each serial section layer. This compromise is due to both the amount of labor involved (the human aspect) and the problems of storing and properly registering the images once they have been obtained (the computer aspect). Solutions for reducing the amount of labor required and increasing resolution in the thickness direction
were to microtome [30] or to avoid sectioning altogether [33]. Also, 250 images captured at 640 by 480 pixel resolution, quite low by current standards, result in a three-dimensional image set of 75 megabytes. This was a large amount of computer memory in 1980. Another problem was the lack of computer software available to obtain three-dimensional measurements or to even accurately display three-dimensional images. In most of the above cases, three-dimensional results were represented by hand-drawn sketches, graphical plots of length vs. depth, or motion pictures. It was at about this point in time that DeHoff [16] stated, “In its current embryonic state of development, the use of serial sectioning analysis for all but the most rudimentary of measurements is prohibitively expensive and tedious”. Since then, image processing and three-dimensional visualization capabilities have improved to a point where storing and representing three-dimensional images are no longer a severe limitation depending on the sectioned volume. In 1991, Hull et al [34] were among the first to use computer software to construct three-dimensional wire frame drawings of microstructural features, namely titanium prior beta grain sizes and shapes. Brystrzycki and Przetakiewicz [35] used a similar technique to study the sizes and shapes of annealing twins in Ni-2% Mn alloy. A substantial, innovative effort was undertaken by Wieland et al [12] in serial sectioning a recrystallized Al-Mn alloy and simultaneously capturing the crystallographic orientation and location of recrystallized grains using electron backscatter electron diffraction (EBSD) in a scanning electron microscope (SEM)[31].
Three-dimensional representations of data obtained through serial sectioning (either optical, SEM, or EBSD) have continued to improve as computer visualization software has advanced[36]. Also, recent developments in digital imaging have significantly reduced the efforts required to perform three-dimensional analyses by eliminating the steps to either digitize or manually trace microstructural features. There have been many other three dimensional analysis experiments, and many more may have been left unpublished due to the historical difficulty of reproducing three dimensional representations onto 2D media. In summary, steady improvements to three dimensional analysis techniques have resulted in semi automated material removal, digital image acquisition, and visualization of three dimensional reconstructions using advanced computer software and hardware[31]. The current development of the focused ion beam, by the author, Michael Groeber, and Michael Uchic, in conjunction with scanning electron microscopy and electron back scattered diffraction techniques has allowed for the sectioning of approximately 40 μm3 of material through completely automated procedures. The arrival of the next generation microscope looks very promising. The microscope developers are working in conjunction with OSU to help develop GUI programs that incorporate a number of analytical techniques into more user-friendly configurations.
CHAPTER 3

Experimental Procedures and Characterization Tools

3.1 Introduction

This chapter discusses the advanced characterization equipment and tools used to perform the work presented in the remaining chapters of this thesis. Additionally, the methods developed and employed for the work presented are described in detail for application of low energy ion milling to TEM sample preparation as well as serial section data collection using a DB-FIB/SEM. Furthermore, image processing routines are described for analysis and reconstruction of acquired, serial section data sets. The thermal history and processing of materials is discussed as well.

3.2 Material Used and Thermal History

A 250 gram sample of Ti-18 Mo alloy used for this research was provided by TIMETAL® company in Hederson, NV. The as-delivered sample was arc arc-melted
using standard arc melting techniques and flipped seven times to increase homogeneity. The button was then encased in cp-Ti packaging, back-filled with Argon, and welded shut. The button was then rolled at 2000 F to further improve homogeneity. The outer packaging of cp-Ti was removed by milling, to leave a button of nominally homogeneous Ti-18 Mo alloy. The as received button was then homogenized in the vacuum furnace at 1100 C for 168 hours and furnace cooled to room temperature.

The resultant button was then partially sectioned into toothpick specimens (1.5 mm x 3 mm x 40 mm) by electronic discharge machining for heat treatments in the ETMT and also 1 cm³ pieces for heat treatments in conventional furnaces. The heat treatments performed are schematically shown in Fig 1. All samples were initially held above the beta solvus to solutionize the material and then rapidly quenched to form athermal omega embryos. Samples were subsequently re-heated to 475 C, ~50 C below the proposed omega solvus, and isothermally held for times of 30 min, 48 hrs and 330 hrs and water quenched to promote growth and coarsening of isothermal omega precipitates.

3.3 Description of Equipments

3.3.1 Mechanical Polishing

Detailed procedures for preparation of specimens for serial section analysis are described in Chapter 4.2.1. All samples for DB-FIB/SEM analysis were polished by traditional metallurgical practices using 600, 800 and 1200 grit Allied[19, 37] SiC paper
on an Allied™ MultiPrep parallel polisher. Finally they were polished with Allied™ 0.5 µm Colloidal Silica suspension. Following polishing, the samples were cleaned with Buehler Ultramet™ sonic cleaning solution, distilled water and ethyl alcohol. Lastly samples were decanted at least 24 hours before inserting in the DB-FIB/SEM.

3.3.2 Scanning Electron Microscope

The scanning electron columns used for this work we incorporated with the DB-FIB/SEM tool. The DB-235 Strata™ and Nova™ NanoLab 600 were equipped with a Sirion type column. The Helios™ NanoLab was equipped with a L-Star column.

3.3.3 Focused Ion Beam

Three generations of DB-FIB/SEM have been used over the course of this thesis to develop the methodologies presented in Chapter Four. The initial machine, DB-235 Strata™ contained a Magnum ion column and mechanical stage. The second generation was the NOVA™ NanoLab 600 equipped with a Sidewinder™ ion column and a Sirion™ electron column. The stage was upgraded to a three axis piezo-electric stage for +/- 2 nm resolution after stage movement. With the advent of the Sidewinder™ ion column, FEI built an ion column with the ability to reduce beam energy to 2 kV. Finally, the latest addition has been the Helios™ NanoLab 600, this system is similar to the Nova™ with a few exception such as the ability to mill at 500 V with the ion column. As
well, the patterning engine has finer resolution and the electron column optics have been improve.

### 3.3.4 Omniprobe™ 200 micromanipulator

The in-situ micromanipulator allows for orthogonal control of a needle inside the DB-FIB/SEM chamber with nm resolution and control. This tool is invaluable for welding pieces of bulk specimen and extracting smaller lamellae. The lamellae can subsequently be welded to any alternative medium, usually a copper or molybdenum Omniprobe™ grid specifically designed for lamellae extraction and thinning.

### 3.3.5 Transmission Electron Microscope

The Philips/FEI CM200™ TEM was used for conventional dark-field imaging and selected area diffraction pattern collection. The CM200™ is a 200kV microscope with a LaB₆ filament.

High Resolution TEM (HRTEM) and High Resolution STEM (HRSTEM) studies were conducted on the FEI Titan™ 80-300 microscope equipped with a Cs corrector for the electron probe. An electron monochromator is attached to reduce the energy spread in the incident probe to 0.15 ev. An ultra high resolution (0.15) ev) electron energy loss spectrometer, and an energy dispersive x-ray spectrometer. The microscope exhibits remarkable performance including an information limit of ~0.07 nm and a resolution of
~0.08 nm in high angle annular dark-field STEM (HAADF, and a spatial resolution for compositional analysis using EELS of ~ 1 nm.

This state of the art microscope provided revolutionary capabilities for characterization down to the angstrom level and atomic resolution imaging of titanium based alloys.

### 3.3.6 Three Dimensional Atom Probe

For 3DAP studies, the site specific samples were prepared using a FEI Nova™ 200 NanoLab. Ideally, 20 um x 5 um x 5 um sections were extracted from the samples using the Omniprobe™ 200 micromanipulator and mounted onto silicon microtips. On each microtip, final specimens of ~3 um in length and ~70 nm tip diameter were prepared by annular ion milling. Subsequently, these samples were used for 3D atom probe tomography studies carried out in an Imago™ local electrode atom probe microscope.

All atom probe experiments were carried out in the electric field evaporation mode at a temperature of 70K, with the evaporation rate varying from 0.2-1.0% and the pulsing voltage at 30% of the steady state applied voltage. The DAVIS™ software was used to collect the data while the IVAS™ software was used to reconstruct and analyze the data.
3.4 Experimental Procedure

3.4.1 Conditions for TEM Lamellae Preparation with Ga⁺ Ions

A FEI Helios equipped with a Sidewinder Ga⁺ liquid metal ion source (LMIS) designed for ion milling from 2 - 30 kV was used for trenching and thinning of site specific TEM samples. Trenches were milled at 30 kV, 21 nA to leave a membrane of material with dimensions of 55 µm across, 3 µm thick and 15 µm deep. The top surfaces of each membrane was coated with a 2 µm protective Pt layer and subsequently extracted, in-situ, using a Omniprobe™ micromanipulator. The membranes were welded to Mo Omniprobe™ grids for thinning, post-processing and TEM analysis.

Rough thinning from 2 µm to ~1 µm was performed at 30 kV 2.8 nA. Final 30 kV thinning was performed at .45 nA and attempted to leave the membrane ~500 nm thick for subsequent, lower energy milling or thin to electron transparency for analysis. All 30 kV milling was performed at 1.4 degrees of incidence using box cut patterns with a dwell time of 100 ns.

Membranes were milled such that each sample contained 30kV, 5kV and 2kV Ga⁺ milled regions. All 5 kV and 2 kV milling was performed on both sides of the membrane using a box cut pattern with 100 ns dwell time at 5 degree of incidence to achieve electron transparency. Table 3.1 summaries the FIB processed materials and their milling energies. The samples that were Ar⁺ FIB processed were transferred to the Fischione Nanomill for further milling of the lamellae.
3.4.2 Low Energy Ar⁺ Ion Milling Experiments Using a Fischione Nanomill™

Fig. 3.2 (a) is a schematic of the low energy concentrated Ar ion milling system (Fischione Nanomill™) along with a 500V Ar ion image (Fig. 3.2 (b)) showing the sample layout and the milling geometry. A concentrated Ar ion beam source at variable energy range of 50 - 2000 V and beam size of 10 - 12 µm has been employed for the milling process and continuously rastered over the region of interest at relatively low ion beam angles (α = 0° - 15°).

This milling procedure is conducted using moderate ion milling rates (2 nm/min for 20 µm x 20 µm area in Si at 900 V and 15°) and ion beam current density of approximately 2.5 pA/µm². The main purpose of using low energy concentrated Ar⁺ ions is to remove any kind of surface artifacts such as residual amorphous damage layers in a reasonable time period without sacrificing any electron transparent region from the TEM sample.

In order to achieve this, Ar ion beam administered at various milling voltages, milling angles and milling rates has been applied. The geometry of milling with the Nanomill™ is similar to that of the Helios™ and greatly reduces the possibility of cross contamination caused by external factors such as the supporting Mo or Cu grid. In order to properly align the specimen for milling, the focused Ar ion beam is used with a secondary electron detector for imaging the region of interest. Milling process is achieved
similar to the FIB box milling where 10 – 12 µm size concentrated ion beam is scanned over a selected (20 µm x 20 µm) box area.

3.4.3 Serial Section Data Acquisition in DB-FIB/SEM

The initial serial sections were performed using the commercial software Slice and View™[5](Fig. 3.3). Slice and View™ is an automation program that allows the user to define the parameters of the volume to be milled and image acquisition parameters. It was designed to produce serial sections with maximum resolution by using only beam shifts and no stage movements. The stage in the DBFIB is a mechanical stage and has a resolution of 0.5 microns, after movements, the stage has the ability to relax and drift for approximately 3 minutes. When spacing of 50 nm is needed to accurately reproduce consistent material removal, any stage drift under these conditions can result in the ion beam missing the sample completely or milling more material than desired and making the spacing between slices indeterminate.

Slice and View™ was designed to serial section through no more than 8 microns of material in one session. It is limited to this depth of sectioning due to the maximum amount of beam shift available within the electron column, if sectioning were to proceed further than 8 microns, the area of interest will shift out of the field of view with each successive slice. This necessitated the development of custom scripts that could perform serial sectioning through larger volumes.
The custom script developed uses image recognition software on the FIB to locate a fiducial mark milled at the end of the volume to be sectioned. The distance from the fiducial mark to the end of the finger is defined initially and then subsequently decreased after each slice (Fig. 3.4 (a) and (b)). This allows the user to incorporate stage movements and then accurately and precisely place the next milling box. Essentially, a stage with 0.5 microns of resolution can now be incrementally moved with 50 nm resolution by compensating for stage error with fiducial recognition and electron beam shifts.

One of the most important benefits from using the DB-FIB is reducing the amount of time necessary for completion in order to reduce monetary cost. Sample prep, both in-situ and ex-situ, should be greatly improved with the use of an automated parallel polisher as well as the incorporation of a micro-EDM to rapidly mill out near net shape fingers for serial sectioning. Ideally, this will cut the time per serial section in half by eliminating the majority of manual work as well as eliminating the need to trench out large amounts of material.

3.4.4 Data Set and Image Processing

3.4.4.1 Foreshortening:
The relative orientation of the two columns in the dual-beam FIB is co-eucentic with an angle of 52° and creates a foreshortening of the image obtained using the electron column (both SE and BSE images). The two methods of compensating for this foreshortening are to stretch the images in the y-direction by a factor of 1.269 1/cos(38°), or to compress the x-direction by a factor of 0.788 (cos(38°). The latter is the preferred method so as to avoid introducing artifacts into the data.

3.4.4.2 Image alignment:

There are two general methods by which a serial data set of images can be aligned relative to one another. The first method relies on an reference frame external to the microstructure, such as a fiducial mark or series of marks. The second method performs a cross-correlation function to evaluate two successive images and performed an appropriate image shift based off their m. This method requires the microstructure contain various distinctive features, this is most easily realized in microstructures containing multiple phases. Microstructure should not be strongly textured; for example, a microstructure that contained only one variant of a precipitate oriented parallel to one another would likely result in a poorly aligned stack for further reconstruction.

The reconstructions and visualizations presented in this work have been aligned using xfalign, a cross-correlation function associated with IMOD[38]. The cross-correlations have been effective, given the complex, multi-phase nature of both the β-
titanium microstructures. It should be noted that the Pt cap may be used as an additional independent reference frame, if necessary.

**3.4.4.3 Image Pre-Processing and Segmentation:**

Similar to two-dimensional image analysis techniques incorporating stereology, it is necessary to perform a series of pre-processing steps on the images in the data-set prior to reconstruction and visualization. These steps involve general routines to reduce noise and produce binary (“thresholded”) images as well as more complicated routines involving segmentation. The general routines are common in image-processing tool-boxes. For this work, the Fovea Pro plug-ins for Adobe Photoshop 7.0 (and higher) were used for the noise-reduction and threshold routines. It should be noted that the incorporation of the custom backscattered electron detector resulted in higher-quality, better contrast images.

In order to threshold the SEM images of Widmanstätten alpha and allotriomorphic alpha presented in Chapter Five, a recipe of image processing routines were performed to isolate the alpha phase as accurately as possible. A 6 x 6 median filter was initially applied to reduce the overall noise inherent from the acquisition process. (Fig. 3.5 (b) A 150 pixel gaussian blur was then applied and the resulting image was background subtracted from the initial image(Fig. 3.5 (c). This technique was used to eliminate any brightness gradients across the image from SED detector orientation during acquisition. The next filter applied to the image was an adaptive threshold with a 70 x 70 pixel window defining the relative, local background (Fig. 3.5 (d). The filter accurately
determined pixel values relative to the alpha and beta phase and greatly increased segmentation effectiveness.

Following application of the adaptive thresholding filter, a euclidian distance map (EDM) erode filter of two pixels was applied to reduce thresholding artifacts shown in Fig. 3.5 (e). Furthermore, it was determined that rejecting all features less that 700 pixels reduced all residual thresholding artifacts(Fig. 3.5 (f). Finally, an EDM dilation of two pixels was used to reverse the EDM erosion process applied earlier. Table 3.2 provides the recipe applied to the data set analyzed in Chapter Five. Indeed, it is crucial to determine a systematic and standard recipe for each data set so that subjective error is not introduced.

3.4.4.4 Reconstruction and Volume Rendering

Following image processing the individual two dimensional data acquired in the DBFIB must be stacked and interconnected to recover the three dimensional nature of desired features. The share-ware program IMOD, from University of Colorado-Boulder, is a set of image processing, modeling and visualization programs used for tomographic reconstruction and for 3D reconstruction of Electron Microscopy serial sections and optical sections. The package contains tools for assembling and aligning data within multiple types and sizes of image stacks, viewing 3-D data from any orientation, modeling and display of the image files. IMOD was then used to apply contours to the interfaces of the binary images and render surfaces to the 3-D reconstruction through
linear interpolation. The resulting three-dimensional model can be visualized in an interactive manner, with user-control of viewing directions and transparency. Further, 2D slices can be “prepared” on any plane through the volume, and attributes of features, such as distances, surface areas, and volumes, may be calculated. Additional details regarding this program can be found in its documentation[38].
Figure 3.1: Schematic of Ti - 18wt% Mo heat treatments.
Figure 3.2: (a) Schematic of Nanomill setup, (b) SED image acquired from Nanomill™.
Figure 3.3: Slice and View schematic.

Figure 3.4: (a) SED image of cantelievers prepared for serial sectioning, (b) schematic of canteliever.
Figure 3.5: (a) SED image from serial section data set. The remaining images, (b - f), are shown following image processing filter labeled accordingly.
Chapter 4

Development of Dual Beam FIB-SEM as an Advanced Characterization Tool

4.1 Introduction and Motivation

Initial investigations into serial sectioning and reconstructions using focused ion beam (FIB) systems were based on single beam systems[39-41]. The small chamber DB-FIB, announced in July, 2000 by FEI company, represented the first tool to provide for site-specific TEM sample extraction and preparation as well as provided an opportunity to facilitate the automated collection of serial sectioning data sets by implementing both the ion and electron column to remove and image features of interest.

Characterization tools such as the DB-FIB, which provide for such automated characterization of a volume of material have resulted in a revolution in the manner in which material characterization occurs. Rather than being limited to describing microstructure by a series of average terms, as estimated by the application of stereology to two-dimensional images; direct three-dimensional characterization is feasible. Researchers at the Center for the Accelerated Maturation of Materials (CAMM) and the
Air Force Research Laboratory (AFRL) have collaborated on much of the earliest work regarding the three-dimensional characterization and representation of microstructures. This chapter will present a methodology for serial sectioning of titanium based alloys with a DB-FIB as well discuss a methodology for preparing the optimal site specific TEM foils.

4.1.1 Three-Dimensional, Serial Sectioning Tool

During the course of work for this thesis, the characterization of microstructural features three dimensionally has undergone revolutionary advancements in terms of characterization systems and the development of commercially available visualization software, and analysis methodologies. While scientists have attempted traditionally to characterize some microstructural features from two dimensional images using methods such as ASTM standards and stereological relationships, many microstructural features can only be measured in three dimensions, such as the true size and morphology of microstructural features, the connectivity between features and the number of features[14].

Furthermore, stereological relationships are quite often generated based on assumptions of mathematically, ideal features populating the volume of interrogation due, in large part, to the fact no direct, three-dimensional characterization and analysis existed. Microstructural features clearly do not have simple regular shapes; in order for stereology
to be most effective and accurate it is crucial to have a good understanding of the three dimensional nature of the quantified objects.

Fundamentally, all stereological measures should be validated by three-dimensional analysis to determine if accurate stereological measurements are possible, as well as to optimize and refine current relationships. Indeed, technological advancements in materials characterization has begun to take the first steps towards direct characterization of microstructures, which in turn has and will continue to necessitate the need for novel analysis methodologies. This is where three-dimensional reconstruction with the DB-FIB will be invaluable for automated acquisition of high fidelity data sets along with various other characterization techniques afforded with the combination of an electron and ion column.

The methods developed and presented in this chapter are directed towards serial section image collection with intermittent EBSD collection. High intensity EBSD pattern quality from titanium alloys requires up to 36 times longer dwell time to produce an indexable pattern which currently, makes full, three dimensional EBSD characterization, infeasible from a time and monetary constraint. As discussed in detail in Chapter 2, titanium alloys have a number of complex and interdependent microstructural features that span a range of length scales.

The DB-FIB systems are ideally suited to address the 50 nm - 100 mm regime, so quite often a few EBSD scans throughout an interrogated volume can provide adequate characterization with the range of length scales present in most commercially
implemented alloys. Additionally, the metastable beta matrix often contains nanometer size features that make indexing impossible. Perhaps the greatest obstacle to overcome is the formation of the amorphous damage layer from FIB milling, which acts as a barrier to EBSD pattern formation.

The concurrent development of this technique in conjunction with simultaneous EBSD collection by Uchic, et. al. and Groeber, et. al.[42-48], as discussed in Chapter 2, has been applied to nickel based superalloys as it is an ideal material candidate for readily imaging microstructural features of significance such as grain boundaries. Most importantly, nickel produces well-defined EBSD patterns with very short exposure time. These factors markedly reduce data collection time into more feasible timeframes, i.e. days for nickel alloys as opposed to weeks for titanium alloys. Due to the advanced state of physics based modeling for grain boundary interactions in nickel alloys and other structural alloys, this information is vital to the superalloy community and should be very useful to the computational modelers attempting to simulate such evolutions.

Unfortunately, such is not the case with titanium-based alloys; high quality data collection is not trivial. Essentially, there are few phenomenological models openly available for prediction of mechanical properties in titanium alloys as discussed in Chapter 2. Over the course of this work, a significant effort has been spearheaded by Fraser et. al. involving the development of neural networks in combination with advanced stereological approach using 2-D SEM images[17, 49-54]. Great strides have been made towards developing some level of predictive capabilities in titanium alloy design based
on neural network analysis of microstructural features measured empirically. This analysis required exorbitant man-hours to prepare and characterize all the necessary features for populating a database, but is an excellent alternative in the absence of physics based models for titanium alloys.

The techniques developed and presented in this chapter have been applied and discussed to Widmanstätten alpha lath formation in Ti – 18 wt% Mo and discussed in Chapter 5.

4.1.2 Site Specific HR-TEM Sample Preparation of Metals by Using Low Energy, Focused Argon Beam

Despite significant advances in transmission electron microscopy (TEM), such as implementation of aberration correction and monochromation to improve resolution and characterization performance[55-58], sample preparation is still one of the most crucial steps in determining the quality and precision of results obtained from TEM characterization techniques. The challenge in TEM sample preparation is to prepare specimens that are electron transparent and possess negligible surface damage and roughness. The presence of any surface artifact convolutes the transmitted signal and makes both the interpretation of the image and chemical analysis cumbersome if not impossible[59, 60].

Conventional broad Ar ion beam milling and Ga+ FIB milling are the two most commonly used ion milling sample preparation techniques for plan-view and cross-
Bombarding material surfaces with highly energetic ions or neutral atoms however, results in well-known artifacts in the form of surface amorphization and/or lattice defects[59, 62-65]. For instance, multiple authors have documented 30kV FIB Ga ion beam milling of Si generated a surface amorphization layer that extended ~30nm into the material and lower energy milling (5-10kV) of the sample produced a damage layer of ~5-10nm[62-65]. Likewise, traditional 5kV Ar broad beam milling of Si produced surface amorphous damage layer of comparable thicknesses[66, 67].

The nature of ion irradiation damage varies depending on target material properties. It is proposed by physics based models that covalently bonded materials (i.e. Si and GaAs) form an amorphous layer as result of high-energy ion milling, whereas less structurally ordered materials such as ductile metals (i.e. Al, Cu), manifest ion damage via the accumulation of ion induced lattice defects (point defects, dislocation loops)[68, 69].

Interaction of the ion beam with the target material is believed to create a sequence of dynamic, inelastic collision events. When recoil energies in the recovery cascade fall below a few eV, the remaining energy is dissipated as lattice vibrations or heat (thermal spike) resulting in local melting of the target material. Molecular Dynamics(MD) computer simulations have demonstrated defect production is well described by considering local melting of the target material during the milling process and subsequent resolidification kinetics of the ion induced melt at the solid–liquid
interface[68, 70-72]. Covalently bonded materials are believed to have relatively slower re-solidification kinetics at the solid–liquid interface than metals. This difference in kinetics allows the liquid melt to quench into an amorphous phase, whereas in metallic materials; crystalline structure at the surface is mainly recovered at the expense of forming lattice defects. Both lattice defects and amorphization are undesirable on or near the surface of high energy FIB milled samples; therefore it has been suggested that samples are further processed using lower energy Ar ions to reduce the damage layer[59, 73, 74].

Low energy Ar FIB milling of TEM samples intends to reduce or eliminate the surface damage layer induced by preceding high energy Ga FIB milling. Overall success of this surface treatment for minimizing the amorphous damage depends on gradual reduction of ion beam energy during the milling process. A general rule of thumb for minimal damage after ion milling is to decrease ion beam energy iteratively in order to reduce the production of lattice defect and amorphization but still remove damage induced from higher energy milling in a steady-state manner[59, 62].

A major limitation of this approach however, is maintaining an adequate ion beam current and coherency for feasible material removal while reducing ion accelerating voltage and maintaining a fine probe size. Hence, a new generation of focused ion gun and column design has been extensively developed and employed to achieve an efficient low energy milling process at higher ion beam currents. This chapter will address the potential benefits of using low energy Ga\(^+\) ion and Ar ion milling practices in preparation
of site specific FIB milled TEM samples for conventional TEM, uncorrected and aberration-corrected HR-(S)TEM characterization. The depth and characteristics of the ion damage layer will also be investigated in various materials depending on applied ion beam energy and target material properties.

4.2 Development of Experimental Methods for Novel DB FIB/SEM Characterization

4.2.1 3D Serial Sectioning with a DB FIB/SEM

In order to obtain three-dimensional reconstructions of the highest fidelity; it is necessary to follow rigorous procedures, both ex-situ and in-situ, for the preparation of samples and subsequent reconstructions. These procedures were developed over the course of this work and represent a large portion of experimental work, refined into a streamlined process for ensuring the fastest acquisition of data with optimal fidelity and minimal artifacts. Attention to proper sample preparation from start to finish is critical to obtaining useable data and reducing the overall use of microscope time, which is a direct reduction in monetary cost. Indeed, subsequent post-processing of data sets will also be dictated by the quality of data set collected. As mentioned in Chapter 2, the process of collecting and analyzing three-dimensional data sets is extremely costly from both a monetary standpoint as well as temporal. It is desirable to streamline all steps as much as possible, hence; a summary of the required experimental procedures is necessary. A
detailed description of the procedural steps, as well as rationale for the stringent nature of the experimental methods is described in Chapter 3.

4.2.1.1 Ex-situ Sample Preparation

The goal of ex-situ sample preparation was to prepare a thin, parallel sample with a low damage, SEM quality, polished surface on both broad faces and at least one of the thin faces. Initially, to produce a starting sample, the alloy was sectioned using electrical discharge machining (EDM) to produce a sample with dimensions of approximately 7.5 mm x 10 mm x 2 mm. The EDM was chosen to section the samples due to the machine’s ability to easily make parallel cuts. The residual EDM recast layer was removed from the sample surfaces and edges with 600 grit wet/dry SiC paper to ensure proper initial thickness measurement to calibrate the material removal rate from polishing and provide as flat surface for adhering the sample to the polishing platen. Indeed, much care is needed when adhering the sample to the platen; it is necessary to maintain a flat sample throughout the polishing process in order to prevent wedging the sample overly thin. It was found that the preferred method for mounting a specimen to the polishing platen was using CrystalBond™ in combination with acetone to create as thin a layer as possible between the sample and platen.

Subsequently, the broad faces were polished using precision metallographic techniques with a final polish media of 0.05 µm colloidal silica. This step is crucial to preventing milling artifacts during the image collection process, it was empirically
determined that any surface roughness or contamination on the top or bottom surface created instability in the milling rate and cause curtaining to arise distorting data quality.

The initial face was polished and the sample was then removed, cleaned, measured and re-adhered with polished side down. This allowed for accurate material removal rate to ensure the proper thickness. Samples were polished to a thickness of approximately 60 µm using a traditional TEM disc grinder or an automated polishing unit such as the Allied™ Multiprep Parallel Polisher. Over the course of preparing samples, both methods proved to be capable of producing excellent samples however, care must be taken with each method to ensure that the sample is properly mounted to the platen.

Following this polishing technique, a novel, final polishing step was applied to ensure the thin face did not possess plastic deformation build up or extensive roughness that would defeat the time saving rational for these procedure. The sample was mounted between two glass microscope slides with CrystalBond as shown in to provide stability while polishing the edge down to 0.05 µm colloidal silica. This produced a sample with three, adjacent, SEM polished surfaces.

This technique was also applied site-specifically, discussed in Chapter 5, in the sense that a desired microstructural feature was identified by SEM and subsequently removed from the bulk by electronic discharge machining. The isolated volume was then polished such that the feature of interest was exposed for optimal milling and imaging conditions.
4.2.1.2 Sample Mounting and Loading

Along with the technological advances of various generations of DB FIB/SEM microscopes, the stage and sample holder also evolved. Initially, with the DB-235, polished samples were mounted on a custom machined, 52° back-tilted holder (see Fig. 4.1(a)). The back-tilted holder was desired in order to automate the collection of serial sections in the DB-FIB given the restrictions imposed by the configuration of both electron and ion columns and also permit the mechanical stage to rest in the most stable configuration; 0 degrees of tilt.

The Nova™DB FIB/SEM platform introduced a new sample holder design, shown in Fig. 4.1 (b), as well as 2 nm resolution piezoelectric stages in the x, y, and tilt. This allowed for the stage to move more precisely, as well it was more stable at tilted angles. This led to the development of a pre-tilted stage holder for conventional SEM stubs that was tilted to 36 degrees. All samples were attached to conventional SEM stubs with silver paint to ensure excellent conductivity and prevent charging. Much care was taken to prevent silver paint from adhering above or below the area of interest, Fig. 4.1 (c).

4.2.1.3 In-situ Sample Preparation

A series of in-situ sample preparation steps were systematically repeated to prepare standardized volumes of interest for interrogation. These procedures are
primarily related to the acceleration of serial sectioning and the elimination of artifacts such as curtaining, the result of preferential milling, or shadowing from milling into the materials. After an area of interest is located using the SEM column, a thin layer of platinum (approximately 1-2 µm thick) is deposited on the broad face directly above the area of interest in order to minimize ion damage to the imaging surface, Fig. 4.2 (a) and (b), as well as produce a uniformly smooth surface and reduce curtaining. The Nova™ and Helios™ platforms both have material pattern files that are optimized for depositing Pt. over large areas. The DB-235, however, did not deposit Pt well for large areas, in order to produce uniformly large Pt. deposition regions; the ion beam was defocused slightly. This was found to be vital to consistency of successive image quality.

After deposition of platinum at a rate of 4 pA/µm², a 30 kV 20 nA Ga ion beam was used to remove material surrounding the area of interest, such that a small volume of material remains largely isolated from the remainder of the sample (see Fig. 4.2(a)). In this fashion, the subsequent collection of serial images was accelerated due to the exposed nature of the volume; and the quality of the images was improved. Additionally, as the volume was milled away, it was common to introduce a shadowing effect on the viewing surface if care was not taken to remove the side trenches initially. Finally, the surface that was to be imaged was milled with a cleaning cross section pattern in order to remove any remaining surface artifacts or perturbations that might negatively influence the subsequent imaging.
This final step is often referred to as a “cleaning” step, and typically uses the highest amperage beam that will result in an optimal surface while reducing overall milling time. Typically, with the DB-235, 3-5 nA was the maximum current that would not unwontedly mill away the protective platinum layer. The increased resolution of the Sidewinder column, present on the Nova and Helios platform, increased this usable current to a maximum value to > 20 nA, and greatly reduced the overall time necessary for data collection.

This rigorous procedure prepared the sample for automated milling and image acquisition with Slice and View™ or custom data collection scripts. Both methods were used in this research. However, it should be noted that when custom scripting is desired for serial sectioning, fiducial markers should be placed within the viewing region. (Fig. 4.2 (a)) Such custom scripting is advantageous for the reconstructions of large volumes of material. Indeed, Slice and View™ with the DB-235 was limited to a total of 8 µm of milling before it was necessary to realign the sample, and the Nova™ platform increased electron beam shift range to 14 µm, which allowed for slightly large interrogation volumes. With custom scripting it was possible to incorporate stage movement and subsequently use image recognition software to locate fiducials and accurately place the next milling region. Essentially, using electron beam shift to account for error during mechanical translation of the stage.

4.2.1.4 Serial Sectioning Parameters
As discussed in Chapter 2, the history of three-dimensional analysis in metallographic characterization spans, at least, from 1918 with Forsman's repeated (serial) sectioning effort to probe the three-dimensional nature of pearlite. Projecting the images of each section onto cardboard layers of appropriate thickness enabled solid models of cementite lamellae to be constructed. The luxury afforded by today's technological advancements of the DB-FIB/SEM is a tool with excellent stability and reproducibility, possessing nanometer resolution for imaging as well as milling, along with the ability to automate processes and remove user subjectivity. The fundamental concept of serial section data collection and analysis are discussed in Chapter 2, while detailed experimental procedures and setup for a DB-FIB/SEM is described in Chapter 3.

After the necessary preparations (both ex-situ and in-situ), small volumes of the samples of interest were serially sectioned and imaged using Slice and View™. With the back-tilted holder, it is possible to position the sample such that the broad face is normal to the ion beam and the imaging surface is tilted 38° from the vertical axis of the electron column. (Fig. 4.3) A 30 kV, 1 nA beam was found to be the maximum useable to successively mill approximate 50 nm slices from the viewing surface with the DB-235; the Nova™ and Helios™ platform allow for high-fidelity slices up to 30 kV 6.5 nA. Again, the ability to increase milling current greatly reduces the overall time required for data collection.

Following each mill, the viewing surface was imaged using the SEM column operating at 20 kV 2.4 nA and a novel, custom back-scattered electron detector (BSD)
(Fig. 4.3). Imaging acquisition parameters are material dependent and must be optimized for specific material conditions. Regardless of SEM column settings, the goal is to produce an image with optimum signal-to-noise ratio and contrast variation between phases; resulting in the best digital image for post processing.

4.2.1.4.1 Novel BSD Detector Mount

As discussed in Chapter 2, z-contrast imaging is the most advantageous way to image alpha and beta titanium with a SEM, however, when the imaging surface is tilted 52 degrees, with respect to horizontal it is difficult, if not impossible, to situate the sample within the DB FIB/SEM chamber such that the detector is mounted normal to the imaging surface. Furthermore, FEI does not offer BSD mounting assemblies for FIB models due to danger of making contact with the electron pole piece. This deficiency posed a rather substantial hurdle. A titanium based alloy imaged with the SED detector is shown in Fig. 4.5, with a small dynamic contrast range; signifying weak difference in channeling contrast contributing to the image intensity. The images acquired from the DB-FIB/SEM with the secondary electron detector use approximately 70 of the possible 255 shades of gray; along with this problem is the abundant presence of secondary alpha in the beta region. Since all forms of alpha exhibits the same relative level of contrast, when attempting to threshold alpha from beta, the beta regions are often filled with unwanted, misrepresented alphas. Frequently, the secondary alpha spans from one
lath to another and thus, during thresholding, the actual morphology of the microstructure is misrepresented.

The human brain is powerful enough to identify the two phases even with such a minimal contrast variation. Image processing routines however, are not capable of such a task with the weak relative difference in contrast. In order to overcome this problem, a novel design was machined to attach to the DB-235 FIB/SEM stage (Fig. 4.4) to position the BSD detector in the best position given the geometrical constraints of the chamber. This was a vital step in producing an image of adequate relative contrast variation for the rigorous, image post-processing steps to follow.

4.2.1.5 Image Post-Processing and Visual Rendering

The first post-processing routine that must be applied to all serial section data sets was a cross-correlation function to align all the images in the data set to a relative frame of reference. Inherent in all collected data set are some level of instability. The MIDAS and XFALIGN programs, provided with the IMOD software[38], produced excellent results while quickly aligning images for this work, as well a producing a list of x and y translations performed to each image.

Subsequent to image alignment, noise removal, binary thresholding and image segmentation are a science all their own. Descriptions of the processing routines described below are provided in Chapter 2. The sets of serial images collected were converted to binary images using routines to remove noise and contrast variations
followed by bi-level or adaptive thresholding. General post-processing steps, applicable to all data sets, consists of performing a Gaussian blur and boolean subtract function to produce an even level of contrast across the image. The remaining image processing steps must then be determined on a case-by-case basis.

Indeed, it was not uncommon to modify image processing and thresholding routines multiple times within an individual data set to achieve consistent image quality. Clearly, this practice is not ideal and makes automated post-processing of images impossible with the current level of automation. The introduction of user subjectivity in this process has been discussed earlier and can not be overstated. Inadvertent falsification of data is very possible with improper post-processing, and ultimately all images should be verified against the original data. The overwhelming majority of image processing for this work was conducted using Adobe Photoshop 7.0 in conjunction with routines available in Fovea Pro 3.0, from Reindeer Graphics, Asheville, NC.

A number of commercial visualization and reconstruction packages have been developed in the past 5 years with Aviso™ and BitPlane™ producing the most widely used. Contouring and surface rendering for the majority of work were performed using IMOD 3.7.7.
4.2.2 Methodology Development of Low kV Ar⁺ Ion Milling Prediction for Optimal Surface Preparation for Subsequent Advanced Electron Microscopy Characterization

Traditionally, conventional TEM sample preparation entailed preparing a disc for ion perforation such that a small region near the perforation would possess electron transparent regions. The formation of an amorphous damage layer has been well known since these techniques were developed, however technological advancement of TEM’s has increased resolution limits to the regime where ion damage has become a limiting factor in advanced characterization techniques.

4.2.2.1 On the Effect of 2-30 kV Ga⁺ Ion Milling on Ti-based Alloys

4.2.2.1.1 Ti–6Al–2Mo–2Cr–2Sn–2Zr (62222)

The characteristic of the ion-induced damage was initially investigated on-FIB milled Ti-62222 alloy sample and Fig. 4.6 (a), (b), (c) and (d) show representative electron micrographs taken from the samples Ga ion beam milled at energies of 30 kV, 5 kV and 2 kV. Corresponding BFTEM image in Fig. 4.6 (a) is taken from the 30 kV FIB milled sample and clearly reveals the indication of 30 kV FIB Ga ion damage within the α-Ti laths as dotty image contrast. This characteristic ion damage contrast may be due to a fine distribution of the dislocation loops within the α-Ti laths due to the high-energy ion milling of the alloy. Similar image contrast was observed at finer scale in a 5kV milled sample as shown in Fig. 4.6 (b) and at a lower energy of 2kV there is no evidence
of any ion damage contrast on the BFTEM image revealing a better representation of the microstructure as shown in Fig. 4.6 (c). Gradually reduction of Ga ion energy has resulted in least apparent damage contrast at ion energy of 2 kV in α-Ti. As the Ga ion energy is approximately proportional to the ion induced damage cascade size, reduction in the ion energy has eventually minimized the magnitude of the ion damage observed in α-Ti. However, detailed investigation of the edge (sidewall) of the α-Ti lath using HRTEM imaging indicates that there also exist a 5nm thick amorphous layer due to the FIB Ga milling of the TEM sample at 2 kV ion energy as shown in Fig. 4.6 (d). Amorphous damage layer in Fig. 4.6 (d) is not unexpected since the bonding in transition metals such as in Ti exhibits both nearly free electron (metallic bonding) and also directional covalent bonding characteristic, ion damage in these materials might as well consist of both apparent lattice defects and a surface amorphous layer[75]. This amorphous damage layer in α-Ti can be further diminished by low energy Ar ion milling of the sample at energies of less than 2 kV.

4.2.2.1.2 EBSD analysis of Si, Al and α-Ti

Indeed, during the process of developing a methodology for three-dimensional, serial section data sets, as described earlier in this chapter, the simultaneous collection of EBSD data was desired. 30 kV Ga⁺ FIB milling, however, resulted in non-indexable patterns as shown in Fig 4.6 (a). This was found to be consistent for a number of Ti-
based alloys systems and made serial section EBSD data sets impossible due to the overwhelming time required to collect and lack of usefulness.

The results presented in the preceding section indicated some form of “damage layer” was removed to enhance image contrast. Along this same line, it was proposed that lower energy milling of 30 kV Ga\(^+\) ion milled surfaces should reduce the “damage layer” and increase EBSD pattern intensity. A series of EBSD patterns taken from 30 kV, 5 kV and 2 kV FIB milled surfaces are shown in Fig. 4.6 (a), (b), (c) for Si, (d), (e), (f) for Al and (g), (h), (i) for \(\alpha\)-Ti (in Ti62222 alloy), respectively. It is apparent from these images that the EBSD patterning quality improved significantly in all three materials by the gradual reduction of the Ga\(^+\) ion milling energy from 30 kV to 2 kV. However, at given FIB ion energy Al exhibits a better pattern quality than those for Si and Ti, whereas Si and Ti both respond similarly to the reduction in the Ga\(^+\) ion energy. This may suggest that relative surface regularity or crystalline structure of the Al has been preserved at even high ion energies as compared to that of Si and Ti, while in these materials a characteristic amorphous damage layer often is formed due to the high-energy ion milling. It should also be noted that Al possesses an isotropic metallic bond, while Si is covalently bonded. Ti, while considered metallic, possesses a significant amount of directionality in bonding due to the asymmetry of the lattice.

4.2.2.1.3 Ti – 6Al – 4V
Recently, advanced high-resolution atomic column imaging and high spatial resolution microanalysis of the FIB prepared samples has been highly regarded for site-specific characterization of the TEM samples, especially after the utilization of aberration corrected microscopy. Therefore, sample surface preparation for this state-of-the-art analysis is more demanding in terms of ion damage tolerance and requires additional cleaning steps through the applications of low energy ion milling practices. The influences of such low energy Ar ion milling process in reduction of ion damage have been evaluated on the FIB cut Ti-6-4 alloy. In Ti-6-4 sample, the change at edge of the FIBed lamellae during the ion milling process was examined and linked to the far edge imaging of the TEM samples. HRTEM images in Fig. 4.8 (a), (c) and (e) shows the progress at the edge of the foil after successive milling stages. As shown in Fig. 4.8 (a) the initial 30 kV Ga milling has left a surface damage layer of about 28 nm in thickness. Following 2 kV low energy Ar milling reduced this damage layer down to thickness of ~5nm (Fig. 4.8 (c)).

It is clear that the low energy Ar ion milling process at 2kV has successfully reduced the amorphous damage layer generated by the 30kV Ga milling process. Further milling of the sample at 500V produced the least damaged sample (≤2nm) where in some areas crystalline lattice regions were extended to the edge of the sample, as shown in Fig 4.8 (e). The characteristic of the damage layer in α-Ti has required a low energy-milling step at 500V so that the crystalline parts of the sample can be studied without any visible amorphous artifacts. These results were also confirmed by the HRTEM images taken
from the far edge of the foil at different ion milling energies. Fig. 4.8 (b), (d) and (f) shows the improvement in HRTEM imaging of the α-Ti lattice structure in the same alloy after the milling stages at 30 kV FIB Ga ion milling, 2 kV and 500V Ar ion milling. The surface mottling seen in Fig. 4.8 (b) due to the 30 kV FIB damage was reduced by Ar ion milling at 2kV as shown in Fig. 4.8 (d) and final 500 V milling (Fig. 4.8 (f)) removed the most of the amorphous damage resulting a definite representation of the periodic lattice structure in the material.

4.2.2.2 Predictions amorphization depth

The gradual reduction in the ion milling energy is intended to remove the amorphous damage layer created by the preceding milling process. The Ar ion milling energy for 30kV FIB finished surfaces was initially set to 2kV and then 500V on the samples that were HRTEM imaged. A final 900V polishing applied on the sample probe-corrected STEM imaged. 900V and 500V milling was carried out as the lowest Ar ion energy for the removal of the amorphous damage layer from the FIB surfaces of each sample. Similar low energy Ar ion milling experiments were also conducted in the literature at the energy range of 3kV to 120V. For example, Barna et al reported an amorphous layer thickness of 5nm at 3kV and 1nm at 250V for Si and 2.1nm at 1.6kV for GaAs and also did not observe any amorphous layer for GaAs at 250V and for Si at 120V Ar ion milling energies[59, 76].
The thickness of Ar induced amorphous damage that was measured in α-Ti at 2kV was approximately 5nm. The typical 30kV FIB Ga ion damage reported for single crystal Si and GaAs in the literature is approximately 22nm and 16nm, respectively[65, 68]. By the systematic reduction of the Ar ion energy down to 500V, the edge of the α-Ti in Ti64 FIB foil exhibited the least amount of amorphization (≤2nm), which was further confirmed by the HRTEM imaging of the far edge of the sample. The thickness of the amorphous damage layer may vary from sample to sample depending on the composition and structure. However, the preliminary results in this work showed that a remarkable reduction in the surface amorphization of the TEM foils can been achieved by using low energy ion milling practices regardless of the composition and structure of the samples milled.

In addition to these observations, an attempt has been made to estimate the thickness of the amorphous damage layer in GaAs, Si and Ti using TRIM software calculations and amorphous damage predictions were compared with the experimental results reported in the literature and present work. Fig. 4.9 (a), (b) and (c) show the TRIM displacement calculations in GaAs, Si and Ti at different Ga and Ar ion energies and 10 degree beam incidence angle. The experimental amorphous damage depth values were marked as vertical bars at the bottom of the each curve indicating the amount of amorphous damage observed at that particular material and ion energy. The predicted results, open circles, were derived from the intersection of the reported 30kV Ga ion depth values with the displacement curves and extrapolated to the lower ion energies
(dashed lines). As seen in Fig. 4.9 the predicted values for amorphous damage depth agree well with the experimental results from the measurements of GaAs, Si and Ti further confirming the successful reduction of the damage layer at reduced ion energies. Amorphous damage reduction was also observed for GaAs and the depth of damage layer in GaAs was reduced as the ion energy was decreased[65, 68]. However, as seen in Fig. 4.5, the reported amorphous damage thickness for GaAs at different ion energies is to some extent lower than that for Si and Ti whereas both Si and Ti has shown similar reduction in their amorphous damage thickness. These contrary results might be explored considering the typical properties of the milled materials such as ground state cohesive energy ($E_c$); GaAs $E_c = 6.7 \text{eV/atom}$, Si $E_c = 4.7 \text{ eV/atom}$, Ti $E_c = 4.8\text{eV/atom}$ of these materials[77, 78]. It is clear that Si and Ti exhibit comparable cohesive energies, which are both relatively less than that for GaAs. As a matter of fact if the absolute values of these cohesive energies are considered and related to the ability to break the atoms of the solid into metastable amorphous state, one might expect greater amount of damage formation in Si and Ti than in GaAs, since the atomic binding energy for Si and Ti is lower than that for GaAs.

It is interesting to see that both Si and Ti show similar trend in their amorphous damage reduction at varying Ar ion energies and this might as well explain the similarities observed in low kV Ga EBSD patterning of the Si and Ti surfaces. This argument clearly suggests that besides the experimental conditions such as ion energy and ion beam incidence angle employed in the milling process, various material
properties such as the type and strength of the bonding between the atoms in the solid might govern the characteristic of the amorphization in different materials processed under similar experimental conditions. The success and efficiency of the low energy milling process mainly depends on the accuracy and precision of designing an optimum experimental condition; optimum ion energy, ion beam incidence angle and milling time, for a specific interest of material; metal, semiconductor and also preparation for a specific imaging technique; BFTEM, EFTEM, HRTEM or aberration corrected TEM.

4.3 Summary

The inception of small DB-FIB/SEM’s for use in materials science has generated outstanding possibilities for advance characterization of materials from both a site-specific sample preparation device as well as tool for three-dimensionally, serial sectioning experiments. Both of these methods require significant understanding and technical expertise to apply, however the reward for success will reveal new frontiers in the accelerated maturation of materials. The work presented in this chapter described a methodology for three-dimensional collection of Ti-based serial section data sets, as well as other material systems.

Additionally, surface amorphous damage in various metallic materials has been successfully diminished using gradual reduction in ion energy for ion milling practices. Low energy ion milling of two different Ti based alloy; Ti–6–2–2–2 and Ti-6-4 resulted in
reduced damage structure in BFTEM imaging of the $\alpha$-Ti at 2kV Ga ion beam on-FIB and HRTEM imaging of the $\alpha$-Ti at 500V post-FIB Ar ion milling of the samples. Potential benefits of low energy Ar ion milling process below 2kV were investigated on different materials all resulting reduced amount of surface damage and improved high resolution imaging quality in both HRTEM and probe aberration corrected STEM imaging of the FIB samples. The benefit of low energy ion milling is very promising for preparation of delicate high-resolution electron microscopy thin foils from FIB samples. Various experimental parameters such as milling time, voltage and sample geometries will be inspected for different material systems in the future.
Fig 4.10: (a) 52 degree back-tilted holder; (b), (c) FEI delieved SEM stub holder.

Fig 4.11: (a) SED image of cantelievers with and without fiducial marks, (b) schematic showing canteliever features
Fig 4.12: Schematic of columns in DB-FIB/SEM and serial sectioning.

Fig 4.13: Custom built holder for back-scattered electron detector
Fig 4.14: SEM image showing low relative contrast
Fig 4.15: BF-TEM images of alpha lath from Ti-62222 in a Ga FIB milled lamellae after (a) 30 kV, (b) 5 kv, and 2 kV indicating the reduction in black dot damage.
Fig 4.16: EBSD patterns collected from Si, Al and Ti after various Ga FIB milling. (a), (b), and (c) show the improvement of silicon with 30 kV, 5 kV, and 2 kV respectively. (d), (e), and (f) show the improvement of aluminum with 30 kV, 5 kV, and 2 kV respectively. (g), (h), and (i) show the improvement of titanium with 30 kV, 5 kV, and 2 kV respectively.
Fig 4. 17: HR-TEM images showing the milling progress at the edge of alpha laths in FIB lamellae after (a) 30 kV Ga, (c) 2 kV Ar, (e) 500 V Ar milling. Included, images from far edge of FIB lamellae after (b) 30 kV Ga, (d) 2 kV Ar and (f) 500 V Ar ion milling.
Fig 4. 18: TRIM simulation of displacement production for (a) GaAs, (b) Si, and (c) Ti at various incident ion beam energies
3-D Study: Precipitation of Allotriomorphic $\alpha$-Ti on Prior $\beta$ Grain Boundaries and Formation of $\alpha$ Side-plates in Titanium Alloys

5.1 Introduction and Motivation

In high strength, two-phase beta titanium alloys, soft regions along beta grain boundaries are notorious in microstructures widely applied in engineering practice and it is crucial to characterize this phenomenon in order to accelerate titanium modeling and understanding. The aforementioned soft regions are believed to form by continuous alpha layers precipitating preferentially at beta grain boundaries. These allotriomorphic alpha layers lead to significantly softer zones along the boundaries as compared with the surrounding aged beta matrix. In conditions with large, equiaxed beta grains, a preferential deformation in the soft layers can have a negative effect on properties such as ductility and fatigue crack nucleation, depending on the actual strength difference.
between the matrix and grain boundary region. In attempts to counteract this effect, various thermo-mechanical treatments may be applied depending on alloy application.

One possible thermo-mechanical treatment to prevent softening is slow cooling of the alloy from above the beta transus and isothermally holding in the alpha + beta phase field. It is known in solute rich, binary Ti-Mo alloys that slow cooling from above the beta transus to a temperature high in the α/β phase field will result in grain boundary allotriomorph precipitation, followed by Widmanstätten alpha growth. It has been proposed by Lee and Aaronson that for the case of grain boundary alpha precipitates, the morphology of an alpha precipitate is determined by the influence of the grain boundary and the conjugate beta grains. It is believed that if precipitates nucleate at a grain boundary, the precipitate forms with as small an angle as possible between the habit plane and grain boundary plane, since this leads to the smallest nucleation energy.

In addition to forming the basis for many of the important beta-Ti alloys (e.g., Timetal-21S, Timetal-5553, Timetal-550, Ti-6246), the binary Ti-Mo system offers many unique advantages as a model alloy system for facilitating three-dimensional FIB interrogation. Specifically, the alloy system exhibits a broad range of microstructures, and molybdenum diffusivity retards the coarsening of the alpha laths, producing microstructural features that fall within the size-scale of the FIB serial section regime. Moreover, the difference in average atomic number between alpha and beta titanium...
phases enhances the relative Z-contrast variation observed in back-scattered electron micrographs.

This chapter will focus on determining the interconnectivities and factors affecting the formation of the allotriomorphic alpha phase on prior beta grain boundaries and the consequent development of alpha side plates from the allotriomorphs through three-dimensional analysis in conjunction with EBSD. Multiple studies have been performed on grain boundary alpha precipitation in titanium alloys using orientation imaging microscopy (OIM) in the scanning electron microscope to provide crystallographic data, coupled with back-scattered electron imaging[84-89]. It is clear from these studies that the prior beta grain boundaries can be decorated with allotriomorphic alpha belonging to different crystallographic variants and Widmanstätten side plates forming from these allotriomorphs could belong to the same variant or a different variant. Various morphologies of the allotriomorphic alpha phase are possible as well, and it is believed that the phase may form a relatively continuous wetting layer along the grain boundary. Conversely, the allotriomorphs also can appear discontinuous at times. Even for the case of a continuous allotriomorph layers, it is necessary to characterize adjacent allotriomorph precipitates to determine if they belong to the same variant or different variants.

A more quantitative measure of the variant selection mechanism was proposed by Bhattacharyya et al.[85]on the basis of electron backscatter diffraction measurements from colonies formed in an alpha/beta Ti alloy. In this work [85] it was repeatedly
observed that the alpha plates grew from a prior beta grain boundary with their alpha\{0001\} pole parallel with the common \{110\} pole of the two adjacent b grains. Furthermore, Stanford and Bate found that this variant selection mechanism could be used to model the transformation texture in Ti–6Al–4V with reasonable accuracy\cite{89}.

The reason why this variant selection rule is not strictly obeyed is still, not yet understood.

Moreover, the formation of Widmanstätten plates from the allotriomorphic alpha phase remains a matter of some controversy. On one hand, it has been suggested that an instability, following Mullins and Sekerka\cite{90}, occurs at the interface between the grain boundary alpha and the adjacent beta grain, which leads to the development of these plates. On the other hand, arguments have been made on the basis of sympathetic nucleation of these plates\cite{89, 91}. However, still the detailed mechanisms of Widmanstätten alpha nucleation still remains an unresolved issue. While it is generally understood that the formation of Widmanstätten plates is influenced by crystallographic effects, such as the adoption of the Burgers orientation relationship, it has been argued that the nucleation of alpha plates in colony microstructures is always at the interface of the allotriomorphic grain boundary alpha\cite{85}.

In 1948 Dube \cite{92, 93} determined from many observations of two-dimensional, optical microscopy sections taken from isothermally transformed alloy steels; that the cross sectional shapes of proeutectoid ferrite precipitates in these alloy steels fall into a few general categories. Subsequently, Dube developed a morphological classification
system based on these observations as discussed in Chapter 2. Later, Aaronson [94] modified Dube's classification system to distinguish between primary Widmanstätten precipitates that grow directly from grain boundaries, and secondary Widmanstätten precipitates that nucleate upon and grow from other precipitates already formed at the grain boundaries. Aaronson [20, 26] proposed that these morphological classifications are general to products of diffusional nucleation and growth transformations in a wide variety of alloy systems.[31, 95]

For the case of binary Ti-Mo, it has been inferred from two-dimensional images, that the alpha phase is believed to decorate prior beta grain boundaries and Widmanstätten alpha lath growth occurred in the vicinity of the allotriomorphic alpha.[80-82, 96, 97] It should be noted that Widmanstätten alpha and allotriomorphic grain boundary alpha frequently do not intersect in two-dimensional, microstructural images. Indeed, if Widmanstätten alpha maintained a distance from the allotriomorphic alpha, it could be assumed that a precipitate free zone of some nature was present. However, a two–dimensional image does not provide sufficient evidence that the Widmanstätten alpha plate nucleated from an event other than the allotriomorphic grain boundary. Quite possibly the reason for the separation of the two phases is due to a sectioning effect. The development of novel three dimensional characterization techniques described in Chapter 4 in conjunction with EBSD is ideal to address the interconnectivity of grain boundary alpha allotriomorphs and Widmanstätten alpha laths as well as probe their respective crystallographic relationships.
The three-dimensional nature of microstructural features, particularly precipitate shape, plays an essential role in the present understanding of microstructural evolution and phenomenological modeling. For example, predictive growth models of grain boundary precipitates [19, 37] and Widmanstätten precipitates [21, 22], along with current phase field modeling [23] depend upon assumed or deduced three-dimensional morphologies of precipitates. The influence of precipitate shape on mechanical properties is also well established [24]. For example, elongated plate or needle-shaped ferrite precipitates can be deleterious to fatigue strength and fracture toughness [25]. No matter what phenomenon, morphology, or characteristic is modeled, physical or experimental evidence is always needed for validation of the model.

5.2 Experimental Procedure

The sample chosen to validate the FIB based, three dimensional serial-sectioning technique developed in Chapter 4 was Ti-18wt% Mo, beta solutionized at 900 C for 1 hr; cooled to 650 C at 50 C per min and isothermally held at 650 C for 3 hours.

The heat treated sample was prepared for sectioning and sectioned as discussed in detail in Chapter 3 and 4. Post processing and reconstruction of the collected data set was performed as described in Chapter 3.
5.3 Results and Discussion

The initial SEM micrograph from the as collected, serial section data set, shown in Fig. 5.1 (a), contains grain boundary allotriomorphs and Widmanstätten alpha laths. It is clear from this image that Widmanstätten alpha has nucleated preferentially into the two different beta grains and furthermore, the majority of the Widmanstätten alpha showed no intersection with the allotriomorphic grain boundary alpha. A discontinuity of the allotriomorphic grain boundary alpha was also contained in Fig. 5.1(a).

In order to elucidate the crystallographic nature of these microstructural features, an SEM image, shown in Fig. 5.1(b), is pseudo-colored to represent the two variants of allotriomorphic alpha and Widmanstätten alpha as determined from the pole figures in Fig. 5.2 (a-d). Interestingly, very little scatter was found in the EBSD data and no change in crystal orientation could be observed between allotriomorphic grain boundary alpha and Widmanstätten alpha. Indeed, this is substantial evidence in favor of a Mullins and Sekerka type nucleation at the interface of grain boundary alpha and the beta matrix [90].

The pole figures shown in Fig. 5.2 (a) and (b) represent the Widmanstätten alpha laths (Fig. 5.2 (a)) growing into the left beta grain (Fig. 5.2 (b)). The pole figures shown in Fig. 5.2 (d) and (c) represent the Widmanstätten alpha (Fig. 5.2 (d)) growing into the right beta grain (Fig. 2 (c)). It is noteworthy to point out the two allotriomorphs of grain boundary alpha present in this data set do not appear with their alpha{0001} pole parallel with the common {110} pole of the two adjacent beta grains [85]. Indeed, the adjacent
beta grains do not even share a common \{110\} pole in this data set. Arrows clearly labeled the \{0001\}alpha // \{110\} beta for the left and right grains respectively; showed that allotriomorphic grain boundary alpha adopted crystallographic relationships with the beta grain and Widmanstätten alpha grew into the preferred beta grain with the same orientation relationship.

The first three-dimensional representation of allotriomorphic grain boundary alpha and Widmanstätten alpha lath morphology is given in Fig. 5.3, depicting the complicated, interconnected nature of the Widmanstätten alpha laths with respect to the allotriomorphs. The selected viewing angle was chosen to show the similar morphology of Widmanstätten alpha laths, which was in good agreement with the EBSD data showing only two, distinct variants of alpha were present.

Charactering the morphology of these features from this type of image, (Fig. 5.3), can be somewhat difficult due to the complicated, interconnected nature of Widmanstätten alpha laths with respect to grain boundary alpha. In order to facilitate determination of Widmanstätten alpha laths connectivity to grain boundary alpha, higher magnification images of the interface are shown in Fig. 5.4 (a-d). Two instances of Widmanstätten alpha lath connectivity is clearly marked with arrows in Fig. 5.4 (a) and (c). Fig. 5.4 (b) and (d) shows the same region ~200 nm below the level observed in Fig. 5.4 (a) and (c). At this depth in the sample the Widmanstätten alpha laths shown connected previously, are detached; substantiating that the stochastic nature of Widmanstätten alpha laths nucleation occurred at the grain boundary allotriomorph.
Indeed, careful examination of the Widmanstätten alpha laths indicated that the overwhelming majority of laths had minimal, but confirmed contact with grain boundary allotriomorphs. It must be noted that thresholding and segmentation of these features is not trivial and artifacts of the process will eliminate some connectivities. Extreme caution was given to reduce this artifact as much as possible.
Fig. 5. 5 (a) SEM micrograph of allotriomorphic grain boundary alpha and Widmanstätten alpha, (b) Pseudo-color overlay representing different variants of alpha
Fig. 5. 6 (a) Pole Figure for left grain Widmanstätten alpha, (b) Pole figure for upper grain boundary alpha, (c) Pole figure for lower grain boundary alpha, (d) Pole figure for right Widmanstätten alpha
Fig. 5. 7 First morphological, three dimensional reconstruction of Widmanstätten alpha laths and allotriomorphic grain boundary alpha
Fig. 5. 8 (a), (b), (c), (d): Three dimensional reconstruction showing connectivity of Widmanstätten alpha laths with preferred grain boundary alpha allotriomorphs for Ti-18 wt% Mo
Chapter 6

Characterization of Omega Phase in Binary Ti-18 Mo Alloy

6.1 Introduction and Motivation

This chapter will attempt to characterize uniquely and address the mechanisms by which the omega phase forms in a beta matrix and to what extent omega acts as a heterogeneous nucleation site for the hexagonal alpha phase in binary Ti -18 wt%(9 at%) Mo alloy. As discussed in Chapter 2 the thermodynamically metastable omega phase in titanium alloys typically forms when rapidly cooling the alloy from above the β transus to room temperature. It is believed that these athermal ω precipitates retain the composition of the parent β matrix and form by the collapse of the {111} planes of the bcc phase via a shuffle mechanism [3]. A great deal of work has been performed by a number of authors in a direct attempt to characterize fully the omega phase in titanium alloys.[8, 98] An equal amount of work has been performed toward the theoretical understanding and proposed nature of the mechanism of formation of omega.[80, 81, 99, 100]
The majority of these authors performed this research during the 1970-80s and gathered outstanding data with the equipment and resolution limits available to them. This data has provided the field and modelers with the current level of characterization and understanding. For the work presented in this chapter; state of the art, nanoscale characterization tools such as HRTEM, HR(S)TEM and 3DAP have been applied to various heat treatments of Ti-18 Mo to determine the composition, interface width, structure, and distribution of the omega phase, and also to investigate the role of omega phase on the subsequent nucleation of alpha phase.

The heat treatments were designed such that all samples were held above the beta solutionizing temperature to allow for complete dissolution of alpha and a stable beta matrix. The samples were then water quenched to room temperature. The monotectoid phase diagram in Fig. 6.1 shows β-rich alloys have a potential to form spinodally decomposed regions as well as ω precipitates if exposed to the proper thermal history. While conducting these heat treatments efforts were made to isolate these phenomena in order to better understand the role they play in beta instabilities formation and heterogeneous nucleation sites.

It is known that performing an isothermal hold below the omega solvus leads to growth of omega precipitates. It has been proposed from the current data, both theoretical and experimental, that omega formation and growth takes place in a mixed mode fashion.[10, 12, 101, 102] Furthermore, the partitioning of alloying elements across the ω/β interface and the morphology of ω precipitates may have a substantial influence
on the propensity of these precipitates to act as potent heterogeneous nucleation sites for the equilibrium $\alpha$ phase.[82, 103-106] Although there have been various studies conducted on both athermal and isothermally annealed $\omega$ precipitates, the details of the $\beta \rightarrow \beta + \omega$ shuffle transformation on quenching, followed by partitioning of elements across the $\beta/\omega$ interface on isothermal annealing are not well understood[18, 107, 108]; in part limited by the sophistication of materials characterization tools available at that time.

It has also been argued[98, 109] that precipitation of the omega phase may provide nucleation sites for precipitation of alpha titanium within the interior of beta grains. It is not known whether the composition of the omega phase itself and/or the rejection of solute from coarsening particles plays a role in the observed behavior. The stability of the omega phase, and hence the range of temperatures over which omega nucleates and grows as a function of alloy composition, particularly molybdenum; is not well established. For alloys whose composition is rich in beta stabilizing elements, there is a possibility that phase separation of the beta phase ($\beta \rightarrow \beta_1 + \beta_2$) may occur. If phase separation does indeed occur, the reaction may occur by either a binodal (nucleation and growth) or spinodal decomposition. While the crystal structure of the two phases would be identical; the lattice parameters would be different resulting in strain centers. This would lead to sporadic strain centers for the binodal case or a very fine scale distribution of strain centers for the spinodal case. These strain centers could function as heterogeneous nucleation sites for the alpha phase within the beta matrix.[110-113]. Depending on the overall composition of a beta titanium alloy and the
specific heat treatment experienced by the alloy, it is expected that these different sites may or may not play a substantial role in alpha nucleation.

With previous resolution limits, it has been impossible to uniquely characterize these phenomena in a fashion that validates current theories and also contributes new data that modelers can incorporate. The data presented in this chapter showcases the powerful combination of high resolution TEM and 3DAP when applied to the characterization of nanometer precipitates of omega in a beta matrix. Elucidating such fundamental microstructural features and knowledge, not only encourages development of physics-based mechanistic models for alpha precipitations, but should also facilitate alloy design.

6.2 Experimental Procedure

A 250 gram sample of Ti-18 Mo alloy used for this research was provided by TIMETAL® company in Henderson, NV. The as-delivered sample was arc arc-melted using standard arc melting techniques and flipped seven times to increase homogeneity. The button was then encased in cp-Ti packaging, back-filled with Argon, and welded shut. The button was then rolled at 2000 F to further improve homogeneity. The outer packaging of cp-Ti was removed by milling, to leave a button of nominally homogeneous Ti-18 Mo alloy. The as received button was then homogenized in the vacuum furnace at 1100 C for 168 hours and furnace cooled to room temperature.
The resultant button was then partially sectioned into toothpick specimens (1.5 mm x 3 mm x 40 mm) by electronic discharge machining for heat treatments in the ETMT and also 1 cm³ pieces for heat treatments in conventional furnaces. The heat treatments performed are schematically shown in Fig. 6.2. All samples were initially held above the beta solvus to solutionize the material and then rapidly quenched to form athermal omega embryos. Samples were subsequently re-heated to 475 C, ~50 C below the proposed omega solvus, and isothermally held for times of 30 min, 48 hrs and 330 hrs and water quenched to promote growth and coarsening of isothermal omega precipitates.

Each specimen was prepared for SEM/FIB characterization following normal metallographic procedures; mounting with conductive bakelite and polishing with 600, 800, and 1200 grit Allied™ SiC paper and 0.05 um colloidal silica. TEM foils were extracted using a FEI Helios™ 600 NanoLab and an Omniprobe™ 200 in-situ plucker. The foils were extracted and welded to Cu Omniprobe™ grids for final thinning. All foils were final FIB milled with a 5 kV 81 nA Ga⁺ ion beam. The foils were subsequently milled with 500 ev Ar⁺ ions using the Fischione 1040 nanomill. The exact parameters of TEM sample preparation and the benefits of low energy ion milling are covered in more detail in Chapter 3.

Conventional TEM, selected area diffraction patterns and dark field imaging were performed with a Phillips/FEI CM200™ microscope. High resolution TEM and STEM was performed on a probe-corrected FEI Titan™ 80-300 microscope with monochromator. All HR-TEM images were taken at scherzer defocus.
For 3DAP studies, the site specific samples were prepared using a FEI Nova™ 200 NanoLab. Ideally, 20 um x 5 um x 5 um sections were extracted from the samples using the Omniprobe™ 200 micromanipulator and mounted onto silicon microtips. On each microtip, final specimens of ~3 um in length and ~70 nm tip diameter were prepared by annular ion milling.[114-117] Subsequently, these samples were used for 3D atom probe tomography studies carried out in an Imago™ local electrode atom probe microscope.

All atom probe experiments were carried out in the electric field evaporation mode at a temperature of 70K, with the evaporation rate varying from 0.2-1.0% and the pulsing voltage at 30% of the steady state applied voltage. The DAVIS™ software was used to collect the data while the IVAS™ software was used to reconstruct and analyze the data.

6.3 Results and Discussion

6.3.1 Characterization of Ti-18Mo β Solutionized, Water Quenched Condition

6.3.1.1 TEM

A TEM dark-field image from Ti – 18 wt% Mo; β solutionized at 1000°C for 30 mins and water quenched, Fig. 6.3 (a), clearly shows 3-5 nm size ω precipitates (bright regions) distributed homogeneously throughout the β matrix. The bright striations across
the image are FIB sample preparation artifacts. The corresponding <110> and <113> selected area diffraction patterns are shown as Fig. 6.3 (b) and (c) respectively. In addition to the primary reflections from the matrix β phase, streaked intensity maxima are beginning to form in both the <110> and <113> selected area diffraction patterns; these reflections correspond to the presence of multiple variants of the ω phase.[118-121]

A HR-STEM image of the same specimen, taken along <110> β, is shown in Fig. 6.4 (a) with the first resolved image of embryonic nuclei of omega phase present. Due to the small size scale of the omega in this condition, it is necessary to perform a low-pass filter to remove noise from the raw image as shown in Fig. 6.4 (b). The contrast variations in this image are related to small z-contrast fluctuations, indicative of compositional segregation and the embryonic omega nuclei present in the sample. A higher magnification image of the central omega nuclei is shown in Fig. 6.5 (a) and clearly displays the partial collapse of (111)β and the coherent nature of the ω/β interface. A schematic of the collapse is taken from S. Banerjee and P. Mukhopadhyay for reference.[37]

6.3.1.2 3DAP

3D atom probe reconstruction from the same material is shown in Fig. 6.6 (a) by plotting 92 at% blue, Ti iso-concentration surfaces (or isosurfaces). Clearly, some compositional partitioning and interconnected network exist containing marginally titanium rich regions. In order to explore the statistical relevance of these composition
fluctuations further, the titanium ion data for these specimens were divided into equal size blocks of 100 atoms and the number of blocks was plotted as a function of average block composition to provide a frequency distribution plot of the composition as shown in Fig. 6.5 (a).

As discussed in Chapter 2, the deviation from binomial shown in Fig. 6.6 (a) is indicative of the initial stages of chemical segregation. Analysis of the molybdenum concentration profile though the specimen is shown in Fig. 6.6 (b) and clearly shows 3-5 nm molybdenum fluctuations which is in excellent correlation with the size scale of precipitates shown in Fig. 6.3 (a).

Given the fast cooling rate imposed by water quenching, it is possible that this partitioning is likely a result of a preceding beta phase separation during the quenching process possibly facilitating the formation of omega.

6.3.2 Characterization of Ti-18Mo β solutionized, WQ; 475 C 30 min, WQ

6.3.2.1 TEM

A TEM dark-field image from Ti – 18 wt% Mo; β solutionized at 1000°C for 30 mins, water quenched and annealed at 475°C for 30 mins, Fig. 6.7 (a), clearly shows 20 - 60 nm ellipsoidal ω precipitates distributed uniformly throughout the β matrix. The corresponding [110] and [113] selected area diffraction patterns are shown as Fig. 6.7 (b)
and (c) respectively. In addition to the primary reflections from the matrix β phase, the [113] diffraction pattern clearly shows additional reflections at 1/3 and 2/3 [13β] positions that correspond to multiple variants of the ω phase [3].

HR-TEM images of the same specimen taken along <110>β are presented in Fig. 6.8 (a) and (b), with a jagged ω/β interface clearly marked between the two phases. Interestingly, the morphology of the ω/β interface is composed of diffusional, growth ledges formed as the omega precipitates coarsen which could act as a heterogeneous nucleation site for equilibrium alpha.[3, 122, 123] The full collapse along <111>β to form the fully developed omega structure is shown in Fig. 6.9

6.3.2.2 3DAP

3D atom probe reconstruction from the same material is shown in Fig. 6.10 (a) with titanium atoms represented as blue dots and molybdenum atoms as red dots. The Ti-rich regions in Fig. 6.10 (a), that appear a stronger blue color; potentially correspond to ω precipitates since the ω phase rejects Mo during isothermal annealing [16]. A clearer depiction of the Ti-rich regions is shown in Fig. 6.10 (b) by plotting 92 at% Ti isosurfaces. This renders a visualization in which ellipsoidal-shaped ω precipitates of different sizes and orientations are visible.

For a more detailed analysis of the 3D morphology and composition of these Ti-rich ω precipitates, ten specific precipitates were selected from the ones shown in Fig.
6.11 (b), based on two criteria: (i) most of the precipitate is captured within the reconstructed volume, and (ii) the precipitate is isolated and not connected to any neighboring precipitates. The compositions and other size-dependent structural parameters for these precipitates have been summarized in Table 1[20, 124-126].

These precipitates had a Mo content ranging from 3.3 to 4.4 at% with overall average of 3.92 at%. From the volume and surface area data, the major and minor axis lengths for each particle were calculated by fitting these to an equivalent prolate spheroid (three principal axes defined by a=b<c). The ‘c/a’ ratios showed a variation of 3.3 to 3.9 with an average value of 3.5. Fig. 6.11 (a) and (b) show magnified views of one such precipitate viewed along two orthogonal directions with major and minor axes of 31 nm and 9 nm respectively. Similarly, for a smaller precipitate, shown in Fig. 6.11 (c) and (d), these values were 20 nm and 5 nm respectively.

In order to determine the composition profile across the β/ω interface accurately, an averaged proximity histogram for all the ten precipitates was calculated with a bin size of 0.1 nm [21], and is plotted in Fig. 6.11 (e). The smallest bin size, including a sufficient number of atoms to give a relatively small statistical compositional error bar (included in the plot), was chosen for this purpose. Away from the interface, the long-range Mo concentrations in the β and ω phases were determined to be 11.7 at% and 2.8 at% respectively. Note that the lower value of the long-range Mo concentration in ω (~2.8%) as compared to the average value ~ 3.5%, can be attributed to the inclusion of the near-interface region, relatively richer in Mo, as well as compositional variations within the ω
precipitates (discussed below) in calculating the average composition of a precipitate. Based on this profile, the width of the $\beta/\omega$ interface appears to be $\sim 3$ nm. Fig. 6.12 (a) shows a alternate 3DAP reconstruction along the mid-section of a single $\omega$ precipitate with a 92 at% Ti isosurface.

The compositional change across this precipitate was determined by averaging across a one-dimensional composition cylinder, of 5 nm diameter (shown in Fig. 6.13 (a)), and plotted in Fig. 6.13 (b). The composition of the $\beta$ regions varied from 10 - 16 at% Mo, while the $\omega$ regions fluctuated from 4-7 at% Mo according to this plot. Such spatial inhomogeneities in Mo content within the same $\omega$ precipitate indicate a diffusion-limited coring effect during the growth of these isothermal precipitates.

6.3.3 Characterization of Ti-18Mo $\beta$ solutionized, WQ; 475 C 48 hours, WQ

6.3.3.1 TEM

A TEM dark-field image from Ti – 18 wt% Mo; $\beta$ solutionized at 1000°C for 30 mins, water quenched and annealed at 475°C for 48 hours, Fig. 6.14 (a), clearly shows 70 - 100 nm ellipsoidal $\omega$ precipitates distributed uniformly throughout the $\beta$ matrix. The corresponding [110] and [113] selected area diffraction patterns are shown as Fig. 6.14 (b) and (c) respectively. In addition to the primary reflections from the $\beta$ matrix, the [113] diffraction pattern clearly shows additional, intense reflections at 1/3 and 2/3 [13]$_{\beta}$ positions that correspond to multiple variants of the $\omega$ phase[8].

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6.3.3.2 3DAP

3D atom probe reconstruction from the same material is shown in Fig. 15 (a) and (b) with titanium rich regions represented as blue and molybdenum rich regions as red. Following 48 hours of isothermal aging the omega precipitates have coarsened larger than the useable volume for 3DAP and the entirety of an omega precipitate can no longer be captured. In order to determine the composition profile across the $\beta/\omega$ interface a molybdenum proximity histogram and composition profile are shown in Fig. 16 (a) and (b) respectively. Away from the interface, the long-range Mo concentrations in the $\beta$ and $\omega$ phases were determined to be $\sim$13 at% and 2.8 at% respectively. Note that the Mo concentration in $\omega$ is more uniform throughout the precipitate and there is no indication of diffusional coring persisting after annealing for 48 hours at 475°C. Based on this profile, the width of the $\beta/\omega$ interface appears to be $\sim$ 3 nm.

6.3.4 Characterization of Ti-18Mo $\beta$ solutionized, WQ; 475°C 330 hours, WQ

6.3.4.2 TEM

A STEM image from Ti – 18 wt% Mo; $\beta$ solutionized at 1000°C for 30 mins, water quenched and annealed at 475°C for 330 hours, Fig. 6.17 (a) and (b), clearly shows 70 - 100 nm ellipsoidal $\omega$ precipitates distributed uniformly throughout the $\beta$ matrix as
well as sporadic and stochastic alpha nucleation events. The infrequent occurrence of alpha after 330 hrs of annealing would tend to suggest that omega is not the dominant nucleating agent, but instead a probabilistic event. However, a HR-STEM image, clearly resolving an \( \alpha/\beta/\omega \) interface, is shown in Fig. 6.18 in an attempt to image the nature of the intersection. Indeed, this image is acquired in projection and it should be noted that some form of stereo-microscopy must be employed to verify that in fact all three phases were in direct contact with one another.

6.3.4.2 3DAP

The omega precipitates were again too large to encapsulate as entire precipitates, however alpha was present due to the long isothermal anneal. This allowed for collection of compositional profiles for \( \alpha, \beta, \) and \( \omega \). The compositional change across these various phases was determined by averaging across a one-dimensional composition cylinder, of 5 nm diameter (shown in Fig. 6.18 (a,c,e)), and plotted in Fig. 6.18 (b,d,f). The composition of the \( \beta \) regions varied from 10 - 13at% Mo, while the \( \omega \) regions fluctuated from 3-4 at% Mo and the \( \alpha \) regions fluctuated between 1.5 – 2.5 at% Mo according to these plots.

6.3.5 Characterization of Omega Stability Above Omega Solvus Temperature

6.3.5.1 Upquenching
A TEM dark-field image from Ti – 18 wt% Mo; \( \beta \) solutionized at 1000°C for 30 mins, water quenched and annealed at 475°C for 48 hours, WQ; 600 C for 5 min, WQ Fig. 6.19 (a), clearly shows 3-5 nm \( \omega \) precipitates distributed uniformly throughout the \( \beta \) matrix in the same fashion as Ti – 18 wt% Mo; \( \beta \) solutionized at 1000°C for 30 mins and water quenched shown in Fig. 6.19 (a). The corresponding [110] selected area diffraction pattern is inset in Fig. 6.19 (b) and clearly shows the diffuse omega reflections that are associated with the partially collapsed, quenched omega.

Interestingly, upon upquenching and holding these samples at 600 C followed by water quenching, it can be observed that the omega phase dissolves after aging for 5 minutes, as shown in Fig 6.19, and produced the same omega distribution associated with a simple beta solutioning and water quenching heat treatment. This served to verify the temperature window of the omega solvus for Ti – 18wt% Mo lies above 475 C and below 600 C.

The early stages of alpha nucleation are also visible in the form of sporadic nucleation events shown in Fig 6.20 (a). It should be noted that the density of alpha nucleation events after again for 5 minutes at 600 C is much lower than the density of omega precipitates prior to aging in the alpha + beta phase field. Additionally, the morphology of the intra-granular alpha precipitates shown in Fig 6.20 (b) suggests alpha nucleation occurs from a nucleation and growth, beta phase separation event as discussed by Williams, et al. in the ternary Ti-Mo-Al system.[98]
Furthermore, the density of alpha precipitates increased with increasing aging time as observed in Fig 6.20 (c), indicating that omega precipitates may not play a substantial role towards the nucleation of equilibrium alpha in the case of a binary, low misfit alloy such as Ti-18wt% Mo. Instead, binodal phase separation may act as heterogenous nucleation sites upon which alpha formed and subsequent sympathetic nucleation followed to achieve the final microstructural state.[80-82, 99, 100, 104-106]

6.4 Summarizing Comments

In summary, using HR-TEM, HR-STEM, and 3D atom probe tomography, the distribution, structure, composition, interface width and 3D morphology of omega precipitates have accurately been determined in a low-misfit, binary Ti–18 Mo alloy. Athermal ω precipitates have been proposed to form by a completely displacive (shuffle-based) mechanism upon quenching, thus inheriting the composition of the parent β matrix. [107, 127]This displacive, partial collapse along {111}_β is verified and clearly shown for the first time in Fig. 6. Furthermore, omega appears to maintain coherency with the beta matrix, however the contrast modulations present represent small-scale composition fluctuations. This small-scale fluctuation was also supported by clear evidence for Ti - Ti clustering from the titanium frequency distribution plot.

Subsequently on isothermal annealing, a displacive-diffusional, mixed mode
\( \beta \rightarrow \omega \) transformation mechanism is presumably operational during the growth of these precipitates. It is proposed that the structural component manifests as the displacive collapse of the \{111\} planes of the \textit{bcc} \( \beta \) phase, preceding the diffusional partitioning of the Mo between these two phases. The results from isothermal annealing show that diffusional growth ledges occur after just 30 mins of aging and persist throughout the hold times. The omega structure, however, forms significantly faster than it takes for molybdenum to reach a uniform composition throughout the structure. This is expected since molybdenum is a relatively slow diffuser in titanium[24] and is responsible for compositional coring.

Compositional coring is clearly dominant at short aging times, but as isothermal hold times increase, molybdenum concentration in the beta matrix at the \( \omega/\beta \) interface has been shown to exceed 30 wt\% Mo, approximately 150\% greater than equilibrium concentration. This Mo – rich layer surrounding omega should contain enough beta stabilizer to prevent alpha nucleation from occurring directly from the \( \omega/\beta \) interface. This is supported by the stochastic nature of alpha nucleation in Fig. 6.16 (a); if omega was a potent heterogeneous nucleation site, alpha would decorate a relatively large number omega precipitates.

The experimental results presented in this chapter not only provide the first, direct 3D spatial and compositional information associated with \( \omega \) precipitates at a nanometer resolution, but also have important implications on the physical mechanisms underlying the nucleation and growth of these precipitates as well as the role they play as
heterogeneous nucleation sites in Ti – 18 wt% Mo.
Fig 6.21: Schematic phase diagram of typical beta monotectoid system; analogous to binary Ti-Mo.
Fig 6.22: Schematic of heat treatment schedule for Ti - 18wt% Mo alloy.
Fig 6.23: (a) DF TEM micrograph of as-quenched material, (b) [110] SAD, (c) {113} SAD
Fig 6.24: (a) Unfiltered HR-STEM images, (b) low pass filter applied to (a) reveals embryonic omega nuclei
Fig 6.25: (a) embryonic omega maintaining a coherent interface and partially collapsed, (b) schematic of partial omega collapse.
Fig 6.26: (a) 92% Ti 3DAP isosurface reconstruction; frequency distribution plot; (c) Mo composition profile.
Fig 6.27: (a) DF TEM micrograph showing multiple variants of omega; (b) [110] SAD; (c) [113] SAD
Fig 6.28: HR-TEM images of diffusional growth ledges present at the omega/beta interface

Fig 6.29: HR-TEM image clearly showing the fully collapsed, isothermal omega
Fig 6.30: 3DAP reconstruction of Ti-Mo

(a) 

(b)  

Ti=92 at%
Fig 6.31: Different variants of isothermal omega reconstructed in a,b,c,d; (e) proxigram averaged from 10 isothermal precipitates
Fig 6.32: Mo composition profile thorough an isothermal omega, showing the diffisional coring effect
Fig 6.33: Isothermal omega aged for 48 hrs, (b) inset is the [110]SAD
Fig 6.34: Isosurface reconstruction only capturing partial omega precipitate
Fig 6.35: (a) Mo proxigram; (b) Mo composition profile
Fig 6.36: (a) Possible stochastic nucleation of alpha from omega, (b) high magnification image
Fig 6.37: HR-STEM image of alpha/omega/beta interface clearly showing the three phases
Fig 6.38: (a,c,e) showing cylindrical composition profiles through alpha, beta and omega; (b) chemical composition profile of the respective phases

ω composition ~ 96% Ti, 4% Mo
α composition ~ 98% Ti, 2% Mo

ω/β interface width ~ 2nm
Fig 6.39: Upquenched Ti - 18 wt% Mo showing full dissolution of isothermal omega, inset is the [110] SAD
Fig 6.40: DF image showing the early stages of nucleation (a), (c); (b) BF TEM image, (d) [110] SAD
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<th>Mo Comp.(at%)</th>
<th>Error in Mo Comp.(at%)</th>
<th>Vol. of ppt. (nm)</th>
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<td><strong>30.1</strong></td>
<td><strong>8.5</strong></td>
<td><strong>3.56</strong></td>
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Table 6.1: Composition and raw data for ten precipitates
CHAPTER 7

SUMMARY AND FUTURE WORK

One focus of this work was to develop methodologies for the characterization of titanium based alloys with advanced electron microscopy characterization tools using a DB-FIB/SEM. Two methodologies, one for three-dimensional data set collection and another for site-specific TEM sample preparation were developed and presented in Chapters Four-Six of this work.

Only the beginning of three-dimensional analysis was developed and a basic application and analysis was performed in Chapter 4. The strength of this technique was clearly displayed in reference to the interconnectivity of Widmanstätten alpha with respect to allotriomorphic grain boundary alpha. The crucial need for three-dimensional analysis was shown with this example as well as the care that must be taken when image processing. Indeed, it should be noted that this technique alone cannot determine uniquely whether Widmanstätten alpha nucleated from the allotriomorphic grain
boundary alpha. However, it does definitively show that connectivity exists for all Widmanstätten alpha to grain boundary alpha.

For this work individual EBSD maps were also collected to probe the crystallographic orientations of the various phases. EBSD pattern analysis revealed that both analyzed allotriomorphs maintained the Burgers orientation relationship with only one of the adjacent grains. Furthermore, the Widmanstätten alpha connected to grain boundary alpha only grew into the grain that held the Burgers OR with the respective allotriomorph. Additionally, the lattice maintained the same orientation with no resolvable rotation between Widmanstätten and grain boundary alpha.

The results provided by EBSD mapping in conjunction with morphological representation substantiated the claim that Widmanstätten alpha nucleated from the allotriomorphic grain boundary alpha, if the two nucleated from different events and coalesced; it would be favorable for the two features to possess at least some level of lattice rotation across the alpha-alpha interface. In order to further characterize this site-specific TEM analysis would be useful. If Widmanstätten alpha nucleated from the grain boundary alpha no interface would be expected between the two morphologies.

The second methodology developed using a DB-FIB SEM was optimal, site-specific TEM sample preparation for advanced analytical techniques. It was well known that sample preparation is of the utmost importance when attempting atomic resolution analysis of metallic materials, as well as for any conventional TEM imaging techniques. Additionally, 30 kV Ga\(^+\) ions used for sputtering in commercial DB-FIB systems left a
residual damage layer on the sputtered surfaces, hindering EBSD collection as well as making TEM analysis very difficult, if at all possible. In order to create the optimal specimens for analysis, characterization of the residual damage layer was performed using HR-TEM and HR-STEM to image the damage. In the future, a more detailed understanding of the damage process needs to be developed.

Following characterization of the damage layers, subsequent low-energy ion milling was performed to reduce the higher energy ion milling damage. A correlation was found with the total number of displacements calculated from TRIM with respect to incident ion-beam energy. As presented in Chapter 4, a critical number of displacements can be found from a single damage layer analysis. From this measurement, it is possible with TRIM to predict the depths of the resultant damage layers for other ion beam energies. With this method it is possible to predict the optimal method to remove higher energy ion damage while not milling significantly with a lower energy ion beam.

The application of the site-specific methodology, developed in Chapter Four, was described in Chapter Six, where the structure and composition of omega precipitates in binary Ti - 18 wt% Mo alloy were probed. The atomic resolution images presented in Chapter Six along with the 3DAP data would not have been possible with out the methodologies developed in Chapter Four. The first experimental validation of the atomic structure and growth of omega was accomplished through a combination of HR-TEM and 3DAP. It was shown experimentally that there is mixed-mode transformation occurring during the growth of these precipitates that is diffusion controlled.
Furthermore, during the growth of omega in Ti - 18 wt% Mo a partitioning of solute occurs at the interface increasing the local solute content in excess of 28 wt% Mo. Such a high level of solute would not favor alpha nucleation in the vicinity of the omega/beta interface and reduce the effectiveness of omega as a potent heterogeneous nucleation site.

3DAP analysis also revealed the three-dimensional morphology of omega precipitates for the first time. This is an invaluable piece of information in conjunction with the composition and atomic structure. Future work will most certainly include incorporation of this information into phase field modeling of the system. This work focused on the low-misfit, Ti-Mo system. It is well known that various alloying elements change the misfit of the system and play a large role in the two-dimensional morphology of omega precipitates. It would be useful to create a phase field model with various alloying elements and predict omega morphology and distributions. Furthermore, with the compositional information collected, the effect of omega as a heterogenous nucleation site can be modeled.

Two methodologies for a DB-FIB/SEM have been developed and applied to materials engineering problems in titanium based alloys. It is the hope of this author that the promise of these techniques will be realized fully over the next 10 years. The results presented in this thesis should clearly show the power of these techniques and dictate the need for further refinement and application.
References


46. Groeber, M., D. Rowenhorst, and M. Uchic, Collection, Processing, and Analysis of Three-Dimensional EBSD Data Sets.


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